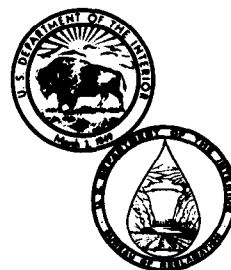# OXIDATION OF FORMALDEHYDE SOLUTIONS USED FOR THE PRESERVATION OF REVERSE OSMOSIS MEMBRANES — PHASE II

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16. ABSTRACT

This report presents the results of the second phase of a two-phase study of a new process for the catalytic oxidation, at ambient temperatures, of dilute formaldehyde used in aqueous solutions for the preservation of cellulose acetate reverse osmosis membranes. The oxidation, involving hydrogen peroxide and an iron (ferric chloride) catalyst, was previously tested in a bench-scale adiabatic reactor to develop test data showing the effect of selected variables (temperature, reactant and catalyst concentrations, and stirring rate) on the oxidation of formaldehyde and formic acid, an intermediate oxidation product. The reaction was shown to be effective in oxidizing formaldehyde solutions, having initial concentrations of between 250 and 950 mg/L, to carbon dioxide and water. Following oxidation, residual formaldehyde levels measured less than 2 mg/L (detection limit of the analytical method used) in the aqueous phase and less than 0.4 mg/m^3 in the carbon dioxide vapor phase. The oxidation was found to be rate controlled rather than mass diffusion controlled.

In the present work, additional adiabatic tests were conducted at a pilot-scale (solution volume 426 times greater than bench-scale) to verify the assumption of direct scale-up for the reactor. In addition, the effects of background salinity, mixing power input, and method of hydrogen peroxide addition to the reactor (metered versus batch addition) were investigated.

An empirical reaction-rate model was developed from a series of isothermal bench-scale tests to predict and optimize the reaction. Parameter estimates and standard errors are presented for the oxidation of methanol (a preservative in the formaldehyde stock solution), formaldehyde, and formic acid, and for the decomposition of hydrogen peroxide. Conclusions are drawn relative to both the optimum pH range for the oxidation and the inhibiting/promoting effects of selected components in the reaction.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS-- *desalination/ *reverse osmosis membranes/ ion exchange/ water purification/ *water treatment/ *formaldehyde oxidation/ formaldehyde disposal/ *membrane preservation/ cellulose acetate membranes/ bacteriostat/ pesticide/ organic oxidation

b. IDENTIFIERS-- Yuma Desalting Test Facility, Arizona/ *Yuma Desalting Plant/ Wellton-Mohawk Irrigation District

c. COSATI Field/Group 07D   COWRR: 0702,0703   SRIM:

OXIDATION OF FORMALDEHYDE SOLUTIONS USED FOR THE PRESERVATION OF REVERSE OSMOSIS MEMBRANES – PHASE II

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UNITED STATES DEPARTMENT OF THE INTERIOR ★ **BUREAU OF RECLAMATION**

ACKNOWLEDGMENTS

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GLOSSARY

LETTER SYMBOLS AND QUANTITIES

A	Formaldehyde concentration
B	Formic acid concentration
b_j	Parameter estimated by nonlinear regression
C_i	Concentration of species i, mmol/L
C_i'	Concentration of species i estimated by numerical integration
%C	Percent carbon (carbon concentration/initial carbon concentration)
E_a	Arrhenius activation energy, kJ/mol
k	Rate constant
r	Rate expression, mmol/(L·s)
R	Gas constant, 0.008314 kJ/(mol·K)
s_i	Estimated experimental accuracy in measuring the concentration of species i
t	Time, s
T	Temperature, °C or K

CHEMICAL FORMULAS

^{14}C	Carbon −14
Ca^{+2}	Calcium ion
Ce^{+2}	Cerous ion
Ce^{+4}	Ceric ion
$CeSO_4$	Cerous sulfate
$Ce(SO_4)_2$	Ceric sulfate
CH_2O	Formaldehyde
CH_2O_2	Formic acid
$CH_2(OH)_2$	Methylene glycol
CH_3OH	Methanol
Cl^-	Chloride ion
CO_2	Carbon dioxide
Fe^{+3}	Ferric ion
$FeCl_3$	Ferric chloride
$FeCl_3 \cdot 6H_2O$	Ferric chloride hexahydrate
H^+	Hydrogen ion
HCl	Hydrochloric acid
HCO_3^-	Bicarbonate ion
H_2O	Water
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfuric acid
HSO_3^-	Bisulfite ion
$KMnO_4$	Permanganate
K_2SO_4	Potassium sulfate
Mg^{+2}	Magnesium ion
Mn^{+2}	Manganese ion
$MnSO_4$	Manganese sulfate
Na^+	Sodium ion
$NaCl$	Sodium chloride
$NaHSO_3$	Sodium bisulfite
$NaOH$	Sodium hydroxide
Na_2SO_4	Sodium sulfate
O_2	Oxygen
OH^-	Hydroxide ion
$R-HSO_3$	Ion exchange resin in the bisulfite form
SO_4^{-2}	Sulfate ion

INTRODUCTION

This report discusses the second phase of a two-phase study of a new process for the catalytic oxidation to carbon dioxide and water of the dilute formaldehyde used in the preservation of cellulose acetate membranes. From these studies, conclusions and recommendations are made for the design and operation of a formaldehyde oxidation reactor for the YDP (Yuma Desalting Plant).

An RO (reverse osmosis) desalting plant is being constructed in Yuma, Arizona, by the Bureau of Reclamation, for treating water from irrigation return flows in the Wellton-Mohawk area. Equipment suppliers for this plant have recommended that RO membranes, when not in use for extended periods, be preserved to prevent microbial attack. One commonly used method under consideration is storage in a 5000-mg/L CH_2O (formaldehyde) solution. Because formaldehyde is a bacteriostat, its use may require a pesticide registration label under FIFRA (Federal Insecticide, Fungicide, and Rodenticide Act) or may be governed by some other Federal or State regulations. In anticipation of these requirements, the Bureau developed and conducted preliminary testing on a neutralization process for disposing of waste formaldehyde solutions [1]. The process uses H_2O_2 (hydrogen peroxide) and dissolved ferric chloride catalyst at a pH of approximately 3.0 to quantitatively oxidize formaldehyde to CO_2 (carbon dioxide) and water in the following series reactions where CH_2O_2 (formic acid) is a temporary intermediate:

$$CH_2O + H_2O_2 \longrightarrow CH_2O_2 + H_2O$$
$$CH_2O_2 + H_2O_2 \longrightarrow CO_2(g) + 2H_2O$$
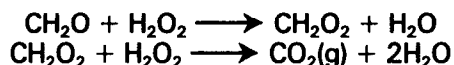
Two additional important reactions that occur during the oxidation of formaldehyde are the decomposition of hydrogen peroxide to oxygen and water and the oxidation of CH_3OH (methanol), which is used as a stabilizer in stock solutions of formaldehyde as follows:

$$2H_2O_2 \longrightarrow O_2 + 2H_2O$$
$$CH_3OH + H_2O_2 \longrightarrow CH_2O + 2H_2O$$
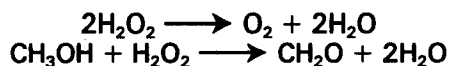
The principal objectives of the earlier studies were (1) to demonstrate that formaldehyde can be oxidized to safe levels; (2) to support a request for a permit under FIFRA; and (3) to provide preliminary design data for a full-scale system at the YDP. Testing was performed using a bench-scale reactor with a solution volume of 250 mL. Both adiabatic (no heat loss) and isothermal (constant temperature) experiments were conducted. Results of the adiabatic tests were used to develop a series of operating curves

to show the oxidation as a function of selected variables (reactant and catalyst concentrations, stirring rate, temperature); whereas, the isothermal test results were used to generate data for fitting a temperature- and concentration-dependent rate expression.

The reaction was shown to be effective in completely oxidizing formaldehyde solutions having initial concentrations between 250 and 950 mg/L. Following oxidation, the residual formaldehyde levels measured less than 2 mg/L (detection limit of the ion chromatograph used for the analysis) in the aqueous phase, and less than 0.4 mg/m³ in the carbon dioxide vapor phase, well below 1.5 mg/m³, the 8-hour TLV-TWA (Threshold Limit Value – Time Weighted Average) adopted by the ACGIH (American Conference of Governmental Industrial Hygienists) [2]. The oxidation was found to be rate controlled rather than mass diffusion controlled and, thus, is highly sensitive to reactant levels and temperature.

Preliminary design recommendations were developed based on thermodynamic calculations for the known oxidations and side reactions, scale-up considerations, and the flushing and disposal requirements of formaldehyde solutions at the YDP. An estimate was also provided of the cost of chemicals used for oxidizing flushings from a single control block (45 m³) at an assumed formaldehyde concentration of 1200 mg/L.

Attempts made at developing a temperature- and concentration-dependent rate expression from kinetic theory were not successful. This was mainly due to the complexity of the reaction mechanism and analytical problems. Both the "initial rate" and "isolation" methods of development were considered. The initial rate method was discounted early because of complications resulting from consecutive reactions and, to a lesser extent, sampling difficulties associated with the technique at the beginning of the reaction. The isolation method could not be used because of the lack of a procedure for measuring hydrogen peroxide during the course of the reaction and difficulties associated with measuring other constituents in the presence of extremely high concentrations of selected reactants. The isolation method was, however, used indirectly to check a proposed mechanism.

The results of experiments and data analysis presented in this report are a continuation of the previous bench-scale testing described above. The ultimate goal of this second phase of testing was to develop design and operating data for the full-scale oxidation system. The overall test objectives were (1) to verify scale-up assumptions for the reactor, which were based on previous bench-scale work; (2)

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[1] Numbers in brackets refer to entries in the Bibliography.

to determine key design and operating parameters for the process; (3) to develop a temperature- and concentration-dependent rate expression for the reaction, both by reevaluating phase I test data and by performing and analyzing a new series of isothermal experiments; and (4) to evaluate the use of bisulfite-regenerated IX (ion exchange) for concentrating residual formaldehyde in water used for flushing RO control blocks.

PHASE II PILOT-SCALE TESTING (ADIABATIC)

Based on the consideration of seven dimensionless parameters for chemical similitude in homogeneous reactions, described by Walas [3], and on an analysis of previous bench-scale oxidation results as a function of power input, it was determined that the reaction rate would not vary significantly with the scale of the reactor. One dimensionless parameter, involving the heat of reaction, becomes important for exothermic reactions; however, this parameter can be ignored for small heats of reaction as experienced with the formaldehyde oxidation (4 to 5 °C at the midpoint conditions). To ensure that the above scale-up assumption was correct, it became necessary to test the oxidation, at the same intensive variable levels, in a larger reactor.

The specific test objectives for the pilot-scale testing were (1) to verify bench-scale similitude assumptions for the scale-up of the reactor, including a reevaluation of the effect of mixing power input; (2) to determine the effects of using Yuma service water instead of deionized water for preparing CH_2O test solutions; (3) to determine operating parameters for the reaction to achieve an acceptable rate and degree of oxidation in an adiabatic environment, given chemical costs and energy input as constraints; and (4) to identify selected key design parameters for the process equipment.

Experimental Apparatus and Test Procedures

The pilot-scale oxidation test equipment is shown diagrammatically on figure 1, and pictorially on figures 2 and 3. Two modified Ravens model M2C FRP (fiber-reinforced plastic), 170-L tanks, fabricated from Dow 411 vinyl ester resin, were used in these experiments. The first tank (fig. 4), equipped with a stainless steel tube heat exchanger and Lightnin model 11 two-speed mixer, was used to prepare formaldehyde solutions and bring them to the appropriate initial test temperatures. The second tank (fig. 5), insulated on the tank wall and base with bonded 2-inch polyurethane protected by a 40-50 mil (1.0-1.3 mm) elastomeric overwrap, was used to contain the reaction. Mixing in this tank was provided by an Eastern model E-2V mixer equipped with a solid-

state, electronically controlled variable-speed drive designed to provide constant torque (versus r/min) over the range of 85 to 1800 r/min. Both tanks had solid boltdown covers with 5-inch (127-mm) PVC (polyvinyl chloride) fillwells for access. The tanks could be completely sealed except for a small clearance around the mixer shafts and a 3-inch (76-mm) vent to an existing building exhaust system. The materials of fabrication for the mixer shafts, fittings, and gaskets were fiberglass, PVC, and neoprene or EPDM (ethylene-propylene diene monomer), respectively.

Temperatures were measured in both tanks using Omega type T (copper constantan) thermocouples with 316SS sheaths. Measurements of pH were made in the reaction tank using a Uniloc model 1002 pH analyzer (fig. 6) with a Uniloc model 399-03-91 combination pH electrode. The temperature and pH signals were processed through a Hewlett Packard model 3421A data acquisition/control system coupled to a Compaq Portable 286 computer, shown on figure 7.

Two methods were used to add H_2O_2 to the reactor depending on the particular test being run: by batch addition, as was done during earlier bench-scale testing, or by metering H_2O_2 to the reactor during the course of the oxidation. The latter method was accomplished using a Masterflex model R-7525-00 digital flow drive (positive displacement roller tubing pump) (fig. 6), which provides both instantaneous flow rate and total flow data in digital form. The 35-percent technical grade H_2O_2 used in this test program was fed directly to the reactor without dilution.

A dilute formaldehyde solution was prepared daily, at one of three concentrations, in the uninsulated "holding" tank by diluting 37-percent industrial grade CH_2O with either deionized or synthesized Yuma service water. The solution was then allowed to hydrate for approximately 24 hours to form $CH_2(OH)_2$ (methylene glycol). Just before initiating the oxidation, the temperature of the solution was adjusted by circulating either hot or cold water through a stainless steel coil in the holding tank to slightly over- or undershoot the desired starting temperature for the test. The solution was then transferred to the insulated reactor where the temperature was monitored until it was within 0.1 °C of the desired starting temperature. At this point, the catalyst ($FeCl_3 \cdot 6H_2O$) and H_2O_2 were added to initiate the test sequence at $t = 0$. After the completion of each test, the holding tank was cleaned and the CH_2O solution for the following day was prepared.

Experimental Design

The dependent variables measured during the course of the reaction were CH_2O concentration, CH_2O_2

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(formic acid) concentration, pH, and temperature. Samples were collected at times of 0, 1, 2, 3, 5, 8, 13, 21, 34, 55, 89, 116.5, 144, and 200 minutes (Fibonacci sequence augmented with two extra sampling times). The independent control variables and associated operating levels (which were the same as those used in earlier bench-scale testing) were as follows:

1. CH_2O concentration, mmol/L: 1.665, 16.65, 31.64
2. H_2O_2 concentration, molar ratio H_2O_2/CH_2O: 4, 6, 8, 10
3. Fe^{+3} concentration, molar ratio Fe^{+3}/CH_2O: 0.2
4. Temperature, °C: 15, 25, 35

The experimental design, shown in table 1, was divided into four segments: the first to verify scale-up assumptions used for the reactor; the second to determine the effects of using synthesized Yuma service water instead of deionized water for preparing CH_2O test solutions; the third to reevaluate the effects of mixing power input in a more controlled test environment (compared with phase I); and the fourth to determine whether improved oxidation could be achieved by metering H_2O_2 to the reactor over time as opposed to batch addition.

Results and Discussion

Scale-Up Verification. – Tests 1-1 through 1-11, shown in table 1, are those associated with reactor scale-up verification. Each test was run with the same "intensive" properties or variable levels (temperature, pH, composition, and energy input) used during 11 corresponding tests in the phase I bench-scale work, but at a considerably larger solution volume: 106.6 L compared with 250 mL for the previous testing, a 426-fold increase. This degree of scale-up was chosen because it represents a multiplicative mean of the solution volumes of the phase I bench-scale reactor and the anticipated full-scale reactor.

The principal basis for comparison of the two series of tests was vested in those tests conducted at midpoint conditions (tests 1-1, 1-4, and 1-8 in table 1). The results of the phase II pilot-scale test 1-8 and the phase I bench-scale test 10 are presented on figures 8 and 9, respectively. Both figures show the change with time in CH_2O, CH_2O_2, and %C (percent carbon of that present at $t = 0$; for these experiments the only source of carbon would be from the original formaldehyde and methanol stabilizer added, or from the oxidation products). In addition, H_2O_2 was measured during test 1-8 (see app. E for a discussion of the analytical methods development for hydrogen peroxide). The variation in temperature and pH for the two midpoint tests are compared on figures 10 and 11, respectively. A typical printout from the com-

puter-controlled data acquisition system for phase II temperature and pH is shown in appendix B.

A comparison of figures 8 and 9 shows that faster oxidation was achieved in the phase I midpoint test. Precise estimates of the disappearance time of CH_2O_2 are difficult, particularly with the phase I data. However, based on a visual interpolation, it is estimated that the times of disappearance are about 77 and 91 minutes, respectively, for phases I and II. This equates to roughly an 18 percent increase in reaction time for phase II. The difference is more pronounced when comparing the disappearance times for CH_2O and %C. Although an attempt was made to keep parameters the same in both tests, there were relatively small variations in temperature and pH, as is shown on figures 10 and 11. The temperature for the phase II test was higher (between 0 and 90 minutes reaction time) by about 0.7 °C, which would tend to accelerate that reaction, not slow it down. In addition, the phase II test was operating in a slightly more favorable pH range for the reaction (discussed in the section entitled "Reaction pH Dependence"): between 2.5 and 2.75. Considering that the remaining intensive properties (composition and energy input) of the tests were the same, and having eliminated pH and temperature as causes for the slower reaction rate, it appears (based on a comparison of figs. 8 and 9) that scale-up does indeed cause the reaction to slow down.

Further comparisons of the two sets of data, at non-midpoint conditions, are shown on figures 12(b), (c), and (d) [the midpoint comparison is repeated on fig. 12(a) for reference]. The "high peroxide" test results, shown on figure 12(c), tend to confirm slower reaction rates (based on the disappearance of CH_2O_2) for phase II, by about 20 percent. However, the "high formaldehyde" and "high temperature" test results presented on figures 12(b) and (d), respectively, show the phase II reactions surpassing those of phase I, yielding faster reaction rates by an estimated 8 and 20 percent. This would suggest, perhaps, that there is less difference in the two sets of data than first indicated by the comparison of the midpoint results.

Figure 8 shows that H_2O_2 disappears shortly after the disappearance of CH_2O_2, although it is added to the reaction in excess of stoichiometric requirements (3-times based on the beginning CH_2O concentration). Based on an analysis of isothermal bench-scale data for the oxidation (discussed in the section entitled "Modeling of Reaction Kinetics"), it was found that the decomposition of H_2O_2 is strongly inhibited by all three organic solutes: methanol, formaldehyde, and formic acid. As the reaction proceeds and the organics disappear, the decomposition reaction proceeds uninhibited.

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Table 1. – Experimental design for pilot-scale testing.

| Test No. | CH$_2$O conc., mmol/L | H$_2$O$_2$ conc., mmol/L | H$_2$O$_2$ addition | | | Fe^{+3} conc., mmol/L | Initial temp., °C | Power input, W/L | Prep. water source |
			Method	Rate, mL/min	Time, min				
1-1*	16.65	99.90	Batch	–	–	3.330	25.0	0.005	DI
1-2	1.665	9.990	Batch	–	–	0.333	25.0	.005	DI
1-3	31.64	189.8	Batch	–	–	6.328	25.0	.005	DI
1-4*	16.65	99.90	Batch	–	–	3.330	25.0	.005	DI
1-5	16.65	66.60	Batch	–	–	3.330	25.0	.005	DI
1-6	16.65	133.2	Batch	–	–	3.330	25.0	.005	DI
1-7	16.65	166.5	Batch	–	–	3.330	25.0	.005	DI
1-8*†	16.65	99.90	Batch	–	–	3.330	25.0	.005	DI
1-9	16.65	99.90	Batch	–	–	3.330	17.1	.005	DI
1-10	16.65	99.90	Batch	–	–	3.330	31.0	.005	DI
1-11	8.33	49.95	Batch	–	–	1.665	25.0	.005	DI
2-1*	16.65	99.90	Batch	–	–	3.330	25.0	.005	YSW
2-2*‡	16.65	99.90	Batch	–	–	3.330	25.0	.005	YSW
2-3*§	16.65	99.90	Batch	–	–	3.330	25.0	.005	YSW
2-4*	16.65	99.90	Batch	–	–	3.330	25.0	.005	10YSW
2-5*‡	16.65	99.90	Batch	–	–	3.330	25.0	.005	10YSW
2-6*§	16.65	99.90	Batch	–	–	3.330	25.0	.005	10YSW
3-1*	16.65	99.90	Batch	–	–	3.330	25.0	.0005	DI
3-2*	16.65	99.90	Batch	–	–	3.330	25.0	.05	DI
4-1*	16.65	99.90	Metered	60.91	15	3.330	25.0	.005	DI
4-2*	16.65	99.90	Metered	30.46	30	3.330	25.0	.005	DI
4-3*	16.65	99.90	Metered	15.23	60	3.330	25.0	.005	DI
4-4	16.65	66.60	Metered	40.62	15	3.330	25.0	.005	DI
4-5	16.65	66.60	Metered	20.31	30	3.330	25.0	.005	DI
4-6	16.65	66.60	Metered	10.16	60	3.330	25.0	.005	DI

*   Midpoint conditions – center point of the experimental region
†   Total carbon (^{14}C) and H$_2$O$_2$ measured
‡   pH adjusted to 4.5 before catalyst addition
§   pH adjusted to 2.7 before catalyst addition
DI   Deionized water
YSW   Yuma service water (synthesized): 300 mg/L
10YSW   10 times Yuma service water (synthesized): 3000 mg/L
W/L   Watts per liter

The rate of oxidation can be increased by strengthening the concentration of either CH$_2$O or H$_2$O$_2$ in the reactor. As figure 13 shows, the time needed for the quantitative oxidation of CH$_2$O solutions varying in concentration from 1.665 to 31.64 mmol/L (50 to 950 mg/L) ranges from well in excess of 200 minutes to less than 55 minutes (Note on fig. 13 that the stoichiometric ratio of Fe^{+3} and CH$_2$O remains constant; therefore, it is difficult to separate the effects of the two variables). Figure 14 indicates a reduction in oxidation time from approximately 144 minutes to less than 55 minutes for a range of H$_2$O$_2$ concentrations between 2 and 5 times the stoichiometric requirement.

The effect of changing initial temperature for the reaction is seen on figure 15. Initial temperature has a major effect on the reaction rate over the range of temperatures investigated (17.1 to 31.0 °C). An increase of only 14 °C shortens the quantitative oxidation time for CH$_2$O from more than 200 minutes to less than 34 minutes. Because most chemical reaction rates increase exponentially with temperature, these results were expected.

Effects of Yuma Service Water Background TDS on the Oxidation. – Tests 2-1 through 2-6, shown in table 1, were performed to determine the effects of background TDS (total dissolved solids), i.e. ionic strength, on the oxidation. Figure 16 shows the oxidation of CH$_2$O and CH$_2$O$_2$ in solutions prepared using synthesized Yuma service water. Similar data are given on figure 17 for tests run with a background TDS equivalent to 10 times the concentration of

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Yuma service water. The service water composition used for preparing the solutions is presented in table 2. Other than for ionic strength and pH, each of the tests represented in figures 16 and 17 were performed at midpoint conditions (see test 1-8 in table 1). Note that, although the following discussion requires observations relating to the effects of pH on the reaction, the main discussions centering on the effects of pH are not presented until later in the report.

Test 2-1 [fig. 16(b)] was performed without pH adjustment. The pH of 6.86, measured before catalyst addition, differed from the 4.63 for the "deionized water" test shown on figure 16(a) simply because of the added salts. This increase in pH caused a significant (approx. 30 percent) increase in the time required for the oxidation of CH_2O_2, presumably because of the effect of the higher pH on the solubility of the iron catalyst. In test 2-2, the results of which are shown on figure 16(c), the pH of the CH_2O solution before catalyst addition was adjusted to a level close to that of the CH_2O solution prepared with distilled water. This resulted in a favorable oxidation rate for CH_2O_2, very close to that for the distilled water test. One additional test at 300-mg/L TDS was run in which the solution pH was adjusted, before catalyst addition, to approximately 2.7 (within the optimum pH range for the reaction of between 2.5 and 2.75; i.e., after catalyst addition). The results, presented on figure 16(d), show a decrease in oxidation efficiency, particularly for CH_2O_2. These tests demonstrate the sensitivity of the reaction to pH.

On figure 17, the same pH dependency seems to be prevalent with test solutions prepared with TDS = 3000 mg/L. The best oxidation results again occur in figure 17(c) where the solution pH was adjusted to near the level of distilled water. It can be seen, however, that the efficiency of oxidation is generally poor with the higher salt background.

Effects of Stirring Power Input on the Oxidation.
– A calibration curve relating torque and revolutions per minute for dilute (low viscosity) solutions was provided by the company that supplied the reaction tank variable-speed mixer. From this information we were able to duplicate, in the present testing, stirring input power levels used during phase I. As shown in table 1, most of the tests were run at a mixing power input of 0.005 W/L (watts per liter), which represents the midpoint condition. Tests 3-1 and 3-2 (table 1) were performed at input power levels a factor of 10 lower and higher, respectively. This was done to further verify previous conclusions regarding the controlling mechanism for the reaction and system scale-up.

During phase I, a series of tests, as described in [1], were run at midpoint conditions with varying stirring

Table 2. – Major ion concentrations in Yuma service water.

	Concentration	
	mg/L	meq/L
Calcium, Ca^{+2}	8.8	0.44
Magnesium, Mg^{+2}	2.7	0.22
Sodium, Na^+	98.1	4.27
Sulfate, SO_4^{-2}	10.2	0.21
Chloride, Cl^-	157.9	4.45
Bicarbonate, HCO_3^-	19.2	0.31
Silica, SiO_2	6.1	–
TDS	303.0	–

power input levels. A correlation between stirring power and total carbon reduction in the reaction was shown to be small [slope less than 0.1 based on a linear fit of the data plotted as the log (1.0 – %C) versus log power]. This indicated that the controlling mechanism for the oxidation was reaction rate, and that mass-transfer effects were relatively unimportant. Figure 18 shows that in the larger pilot-scale reactor similar conditions exist. Although total carbon was not measured during the course of the reactions, it is evident from the CH_2O and CH_2O_2 data that varying the mixing input power over a range of 0.0005 to 0.05 W/L had virtually no effect on the rate of oxidation. This further verifies the assumption of small diffusional resistance made in an earlier chemical similitude analysis for scale-up.

Metered Hydrogen Peroxide Versus Batch Addition.
– An undesirable side reaction that occurs in the catalyzed oxidation of formaldehyde is the decomposition of hydrogen peroxide to oxygen and water. It was thought that this side reaction might be curtailed somewhat by metering H_2O_2 to the reactor as opposed to batch addition. To investigate this theory, a series of tests (4-1 through 4-6, table 1) were run at midpoint conditions in which H_2O_2 was metered to the reactions over periods of 15, 30, and 60 minutes. The results of these tests are compared with those of the batch addition case on figure 19. The results of a similar series of tests in which 2-times stoichiometric H_2O_2 was added instead of the midpoint level of 3-times are shown on figure 20.

Superimposing the four graphs of figure 19 shows that, for both CH_2O and CH_2O_2, the curves on figures 19(b), (c), and (d) (tests in which H_2O_2 was metered) diverge from the corresponding batch addition curves until the end of their respective metering times. When the entire amount of H_2O_2 has been added, the curves again converge. The same is true for the data on figure 20. From this it appears that

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very little, if any, benefit can be attained from metering H_2O_2, either from a rate or stoichiometric standpoint. This conclusion is supported by isothermal data (discussed in the section entitled "Modeling of Reaction Kinetics"), which suggest that the organic solutes significantly inhibit the decomposition of hydrogen peroxide.

REACTION pH DEPENDENCE

To better understand the effect pH has on the reaction, a series of beaker tests were performed to determine oxidation efficiency with time as a function of initial solution pH. Six beakers were filled with 1.0 L of 16.65 mmol/L (500 mg/L) CH_2O, prepared with deionized water, followed by the addition of 3.33 mmol/L of $FeCl_3$ catalyst. The pH of each of the six solutions was then adjusted with 0.05N HCl/NaOH to the following levels: 2.25, 2.50, 2.75, 3.00, 3.25, and 3.50. Finally, 99.90 mmol/L of H_2O_2 was added to each beaker to start the tests. No attempt was made to regulate the temperature of the reactions. The starting temperature was approximately 20 °C. Samples were then collected from each beaker at reaction times of 0, 30, 60, 120, 180, 270, and 360 minutes for CH_2O and CH_2O_2 analysis on the IC (ion chromatography).

The results of the analyses are shown on figure 21. These graphs clearly show, based on the disappearance of CH_2O_2, that the reaction proceeds faster at a pH of about 2.75 to 3.00. At higher pH's the solubility limit of $FeCl_3$ is exceeded, and a precipitate forms which, in effect, reduces the amount of catalyst available to the reaction. At lower pH's the reaction is also retarded; however, the mechanism for this is not fully understood.

The data from these tests were used to select the initial pH levels for the isothermal bench-scale experiments, which are discussed in the next section.

MODELING OF REACTION KINETICS

This section presents results of response surface empirical modeling experiments for estimating the rate of hydrogen peroxide oxidation of formaldehyde storage solution in the presence of a homogeneous ferric chloride catalyst. Two independent sets of data are analyzed: first, previous phase I adiabatic reactor test data to obtain a preliminary reaction rate model; and second, phase II isothermal reactor test data from experiments of this test program. The independent variables for phase II are pH, temperature, and the concentrations of ferric chloride, hydrogen peroxide, methanol, and formaldehyde. The measured response variables are the concentrations of hydrogen peroxide, formaldehyde, and formic acid.

The oxidation of the formaldehyde storage solution to carbon dioxide and water involves four reactions:

1. **Oxidation of the methanol stabilizer to formaldehyde,**
2. Oxidation of formaldehyde to formic acid,
3. Oxidation of formic acid to carbon dioxide, and
4. Decomposition of hydrogen peroxide to oxygen and water.

The reaction rate model consists of four coupled differential equations. In this section these equations are solved by numerical integration to compare calculated with observed concentrations of hydrogen peroxide, formaldehyde, and formic acid. Based on a set of 65 experiments, the empirical model estimates the following for the range of conditions expected at the Yuma Desalting Plant.

1. Reaction rates as functions of pH, temperature, and concentrations of the reactants, ferric chloride catalyst, sodium chloride, and sodium sulfate;
2. Reaction orders (exponents) of the reactants and catalyst (reactions 1, 2, 3, and 4 above);
3. pH for maximum reaction rates (reactions 1, 2, 3, and 4);
4. Inhibiting effect of organic reactants on the decomposition of hydrogen peroxide (reaction 4);
5. Inhibiting effect of sodium sulfate (reactions 2, 3, and 4);
6. Promoting effect of sodium chloride (reactions 2, 3, and 4); and
7. Activation energies (reactions 1, 2, 3, and 4).

Experimental Design

Preliminary Reaction Rate Model. – Data from the phase I adiabatic reactor tests [1] were analyzed to obtain a preliminary reaction rate model for estimating the range of sample collection times for the phase II response surface experiments.

Series First-Order Reactions. – Neglecting oxidation of methanol, which is present in a mole ratio of 0.17:1 methanol to formaldehyde in the industrial grade formaldehyde solution, the oxidation of formaldehyde to formic acid followed by the oxidation of formic acid to carbon dioxide may be described by the differential equations:

$$dA/dt = -k_1A; \qquad \text{At } t = 0, A = A_o \quad (1)$$
$$dB/dt = k_1A - k_2B; \qquad \text{At } t = 0, B = 0 \quad (2)$$

where:

A = formaldehyde concentration,
B = formic acid concentration, and
k_1, k_2 = rate constants that are functions of temperature, pH, catalyst concentration, and hydrogen peroxide concentration.

At constant values of k_1 and k_2, equations (1) and (2) can be integrated to yield:

$$A = A_o \exp(-k_1 t), \text{ and} \tag{3}$$

$$B = \frac{A_o k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] \tag{4}$$

See figure 22 for concentration-time profiles described by equations (3) and (4). Operation at non-constant temperature, pH, or hydrogen peroxide concentration would distort these profiles.

Nonlinear Regression with an Empirical Kinetics Model. – Figure 22 indicates that a series reaction of order one with respect to formaldehyde and formic acid may accurately describe the reaction kinetics. Because of this qualitative similarity between the series first-order reaction and the phase I test results and because of the variation in pH and temperature during each reactor test and the lack of pH data, an exponent of 1.0 for the organic species was assumed in the following empirical power rate equations:

$$f = C_5{}^{b_3} C_4{}^{b_4} 10^9 \exp(-b_5/RT) \tag{5}$$

$$r_1 = b_1 f C_1 \text{ (oxidation of methanol to formaldehyde)} \tag{6}$$

$$r_2 = b_1 f C_2 \text{ (oxidation of formaldehyde to formic acid)} \tag{7}$$

$$r_3 = b_2 f C_3 \text{ (oxidation of formic acid to carbon dioxide)} \tag{8}$$

$$r_4 = 0 \text{ (decomposition of hydrogen peroxide)} \tag{9}$$

$$\frac{dC_1}{dt} = -r_1 \tag{10}$$

$$\frac{dC_2}{dt} = r_1 - r_2 \tag{11}$$

$$\frac{dC_3}{dt} = r_2 - r_3 \tag{12}$$

$$\frac{dC_4}{dt} = -r_1 - r_2 - r_3 - r_4 \tag{13}$$

where:

b_j = parameter to be estimated by nonlinear regression,

$b_1 f$ = k_1 in equations (1), (2), (3), and (4);

$b_2 f$ = k_2 in equations (1), (2), (3) and (4);

b_5 = common Arrhenius activation energy, kJ/mol;

C_i = concentration of species i, mol/L;

C_1 = methanol, CH_3OH;

C_2 = formaldehyde, CH_2O;

C_3 = formic acid, CH_2O_2;

C_4 = hydrogen peroxide, H_2O_2;

C_5 = ferric chloride, $FeCl_3$;

t = time, seconds;

T = temperature, K; and

R = gas constant = 0.008314 kJ/(mol·K).

For lack of methanol data, the rate constant, b_1, for the oxidation of methanol to formaldehyde was assumed equal to that for the oxidation of formaldehyde to formic acid. The catalytic decomposition of hydrogen peroxide, an undesirable side reaction, was assumed negligible, see equation (9). Note that a common activation energy was assumed for the three organic species.

The data set for estimating b_1 through b_5 consisted of phase I reactor tests: 6, 8, 10, 11, 12, 13, 14, 15, 16, 19, 20, 21, 22, 30, 32, 49 (containing measurements for both formaldehyde and formic acid), and 24, 36, 39, and 41 (containing no formic acid measurements). Values of concentration versus time were computed from the initial values (at t = 0) and equations (5) through (13) using IMSL FORTRAN numerical integration subroutine DGEAR [4]. Residual values were computed as:

$$res_1 = \frac{C_2 - C_2'}{C_{20}}$$

$$res_2 = \frac{C_3 - C_3'}{C_{20}}$$

where C_{20} is the initial formaldehyde concentration C_2 at $t = 0$, and C_i' is the concentration of species i estimated by the numerical integration procedure described above. The Marquardt algorithm in SPSS Nonlinear [5] was used to perform the nonlinear regressions.

Regression results are shown in table 3. Although the response variables (formaldehyde and formic acid concentration) were recorded at 12 different times for each test, these multiple observations were not independent, but provided replicate response measurements. All recorded response measurements were used as the data set for the regressions, but the number of independent observations was conservatively considered as the number of tests multiplied by the number of response variables. Thus, the total data set consists of 36 independent observations [16 tests times 2 response variables plus 4 tests times 1 response variable (formaldehyde concentration only)].

Discussion. – At the test conditions of constant pH (approx. 3.3), temperature (25 °C), ferric chloride concentration (3.33 mmol/L), and initial hydrogen peroxide concentration (99.90 mmol/L), the regression-estimated, first-order rate constants

$$k_1 = 2.76 \times 10^{-3} \text{s}^{-1}, \text{ and } k_2/k_1 = 0.38$$

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Table 3. — Regression results of phase I data.

Parameter i	Estimated value of b_i	Standard error of estimate
1	0.1151	0.21
2	0.04374	0.078
3	−0.9045	0.47
4	0.8949	0.45
5	68.3	3.6

Note: Standard errors are estimated based on 31 degrees of freedom.

(see fig. 22 for the concentration-time profiles for formaldehyde and formic acid at constant H_2O_2). The residuals are consistently skewed during the initial portion of each test with observed concentrations lower than those calculated for both formaldehyde and formic acid. This skewness indicates inadequacy of equations (5) through (9) to accurately describe the oxidation reaction. Possible reasons for the poor fit include:

1. The empirical model with power parameters on ferric chloride and hydrogen peroxide may be inadequate.
2. The reactions may be other than first-order with respect to formaldehyde and formic acid.
3. Unmeasured and varying test conditions (e.g. pH) that influence the reaction rate were not included in the model.
4. pH adjustment changed the form of iron catalyst.

Possible reasons for the unexpected negative exponent on the ferric chloride concentration include:

1. Extreme collinearity between the "independent" variables of formaldehyde, hydrogen peroxide, and ferric chloride because the ratios of their initial concentrations were the same for all but a few of the experiments.
2. The assumption of negligible decomposition of hydrogen peroxide may be invalid, see equation (9).
3. Unmeasured and varying test conditions (e.g. pH) that influence the reaction rate were not included in the model.

Experimental Apparatus and Procedures. — The phase II response surface experiments were conducted using 2.0-L test solutions contained in covered beakers, which were submersed to about solution level in a constant temperature bath to achieve isothermal conditions. Test solutions were prepared from a 2-percent formaldehyde stock solution that had been allowed to hydrolyze to $CH_2(OH)_2$ (methylene glygol) at room temperature for at least

24 hours. Tests were run in groups of four with mixing provided by the ganged stirrer paddles of a Phipps & Bird model 300 jar test apparatus.

Tests were initiated by bringing the solutions to equilibrium temperature with the bath. Ferric chloride catalyst was then added to each beaker and the pH of the unbuffered solutions adjusted with either HCl or NaOH to the initial test pH prescribed for each experiment. Finally, after an initial set of samples was collected, the tests were started ($t = 0$) by the addition of H_2O_2. All samples were quenched with excess $NaHSO_3$ (sodium bisulfite) for formaldehyde and formate analysis, and with H_2SO_4 to an acid concentration of 1.0 N for hydrogen peroxide analysis. Samples were analyzed within 4 hours.

Temperature was measured with an NBS certified mercury-in-glass thermometer with a reported accuracy of 0.05 °C. An Orion model 501 pH meter with a combination electrode was used to initially adjust the pH of the test solutions and, subsequently, to make pH measurements. The meter was recalibrated with a pH 2.5, 3.5, and 4.0 buffer before each sampling time, and the temperature compensation was adjusted to the temperature of the reactor. The accuracy of the pH measurements was determined to be 0.05 pH units.

See appendix E for a description of the methods used for determining the concentration of formaldehyde, formate, hydrogen peroxide, and total iron.

Temperature and pH were recorded and samples were collected for concentration measurements of hydrogen peroxide, formaldehyde, and formic acid initially (before the addition of hydrogen peroxide) and at five sampling times after the addition of hydrogen peroxide. Two optimum sampling times for the measurement of formic acid were estimated based on the method of Box and Lucas [6], the preliminary reaction rate model developed from phase I data, and the following (erroneous) assumptions:

1. Reaction rates are independent of ferric chloride concentration;
2. Reaction rates are independent of pH; and
3. Concentrations of excess reactants remain constant at their initial values.

To include additional earlier sampling times for formaldehyde measurements and to compensate for the above assumptions, the two optimum sampling times were bounded by two earlier and one later additional sampling times.

All reagents used were ACS (American Chemical Society) reagent grade, except for the industrial grade formaldehyde, which was purchased in bulk for the

adiabatic pilot-scale testing. The formaldehyde specifications closely matched those planned for the Yuma Desalting Plant. The specific gravity of the formaldehyde was measured to determine initial methanol concentration.

Experimental Conditions. – Tables 4 and 5 list the eight independent variables and their specified values at the beginning of each of the 65 experiments. Concentrations of ferric chloride, sodium chloride, and sodium sulfate salts were constant for each experiment. The +1 level for sodium sulfate simulates a formaldehyde removal ion-exchange regeneration solution containing 2.5 percent sodium bisulfite that has been air-oxidized to sodium sulfate (see section in this report entitled "Bisulfite-Regenerated Ion Exchange Testing"). Temperature and pH were approximately constant for each experiment. The midpoint pH level was selected based on the results discussed in the previous section in this report entitled "Reaction pH Dependence." The low midpoint formaldehyde concentration of 50 mg/L was selected to accomplish the following:

1. Model and maximize oxidation rates at low formaldehyde and formic acid concentrations where the oxidation rates are slowest; and
2. Extrapolate oxidation rates outside the experimental range down to disposal concentra-

tions of 1 mg/L for formaldehyde and formic acid (in measuring formic acid concentrations with the ion chromatograph, the adjacent chloride ion peak was expected to prevent the detection of formate ion concentrations below 5 mg/L).

Reaction Rate Model

Four irreversible reactions are assumed for the hydrogen peroxide oxidation of formaldehyde solution in the presence of ferric chloride catalyst:

1. Oxidation of methanol stabilizer to formaldehyde and water
   $$CH_3OH + H_2O_2 \longrightarrow CH_2O + 2H_2O$$
2. Oxidation of formaldehyde to formic acid and water
   $$CH_2O + H_2O_2 \longrightarrow CH_2O_2 + H_2O$$
3. Oxidation of formic acid to carbon dioxide and water
   $$CH_2O_2 + H_2O_2 \longrightarrow CO_2\uparrow + 2H_2O$$
4. Decomposition of hydrogen peroxide to oxygen and water
   $$2H_2O_2 \longrightarrow O_2 + 2H_2O$$

The following empirical reaction rate model was used to describe the rates of the above four reactions:

Table 4. – Initial values of independent variables for isothermal bench-scale testing.

Variable	Units	Level					
		−2	−1	0	+1	+2	+3
pH (unbuffered)		2.25	2.50	2.75	3.00	3.25	
Temperature	°C		15.0	25.0	35.0		
Ferric chloride hexahydrate, $FeCl_3 \cdot 6H_2O$	mmol/L mg/L		0.3 81.1	1.0 270.0	3.0 811.0		
Hydrogen peroxide, H_2O_2	mmol/L mg/L		3.33 113.0	10.0 680.0	33.3 1130.0		
Methanol, CH_3OH	mmol/L mg/L		1.11 35.6	3.33 107.0	11.1 356.0		
Formaldehyde, CH_2O	mmol/L mg/L		0.0 0.0	1.67 50.0	16.7 500.0		
Sodium chloride, NaCl	mmol/L mg/L			0.0 0.0	6.0 350.7		
Sodium sulfate, Na_2SO_4	mmol/L mg/L			0.0 0.0	0.5 71.0	10.0 1420.0	200 28,400

Note: A mole ratio of 0.17 to 1 methanol to formaldehyde in the methanol-stabilized industrial grade reagent produces initial methanol concentrations of 0.0, 0.295, and 2.95 mmol/L at initial formaldehyde levels of −1, 0, and +1, respectively.

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Table 5. — Initial conditions of the isothermal bench-scale experiments.

Test No.	Initial pH	Initial temp., °C	FeCl$_3$ conc., mmol/L	H$_2$O$_2$ conc., mmol/L	CH$_3$OH conc., mmol/L	CH$_2$O conc., mmol/L
1	3.00	35	1.00	10.00	0.29	1.67
2	3.00	15	1.00	10.00	.29	1.67
3	2.50	35	1.00	10.00	.29	1.67
4	2.50	15	1.00	10.00	.29	1.67
5	2.75	25	3.00	33.30	.29	1.67
6	2.75	25	3.00	3.33	.29	1.67
7	2.75	25	0.30	33.30	.29	1.67
8	2.75	25	0.30	3.33	.29	1.67
9	2.75	35	1.00	10.00	2.95	16.70
10	2.75	35	1.00	10.00	0.00	0.00
11	2.75	15	1.00	10.00	2.95	16.70
12	2.75	15	1.00	10.00	0.00	0.00
13	3.00	25	3.00	10.00	.29	1.67
14	3.00	25	0.30	10.00	.29	1.67
15	2.50	25	3.00	10.00	.29	1.67
16	2.50	25	0.30	10.00	.29	1.67
17	2.75	25	1.00	33.30	2.95	16.70
18	2.75	25	1.00	33.30	0.00	0.00
19	2.75	25	1.00	3.33	2.95	16.70
20	2.75	25	1.00	3.33	0.00	0.00
[1]21	2.75	25	1.00	10.00	.29	1.67
[1]22	2.75	25	1.00	10.00	.29	1.67
[1]23	2.75	25	1.00	10.00	.29	1.67
24	2.75	35	3.00	10.00	.29	1.67
25	2.75	35	0.30	10.00	.29	1.67
26	2.75	15	3.00	10.00	.29	1.67
27	2.75	15	0.30	10.00	.29	1.67
28	3.00	25	1.00	33.30	.29	1.67
29	3.00	25	1.00	3.33	.29	1.67
30	2.50	25	1.00	33.30	.29	1.67
31	2.50	25	1.00	3.33	.29	1.67
32	2.75	25	3.00	10.00	2.95	16.70
33	2.75	25	3.00	10.00	0.00	0.00
34	2.75	25	0.30	10.00	2.95	16.70
35	2.75	25	0.30	10.00	0.00	0.00
36	3.00	25	1.00	10.00	2.95	16.70
37	3.00	25	1.00	10.00	0.00	0.00
38	2.50	25	1.00	10.00	2.95	16.70
39	2.50	25	1.00	10.00	0.00	0.00
40	2.75	35	1.00	33.30	.29	1.67
41	2.75	35	1.00	3.33	.29	1.67
42	2.75	15	1.00	33.30	.29	1.67
43	2.75	15	1.00	3.33	.29	1.67
[1]44	2.75	25	1.00	10.00	.29	1.67
[1]45	2.75	25	1.00	10.00	.29	1.67
[1]46	2.75	25	1.00	10.00	.29	1.67
47	3.25	25	1.00	10.00	.29	1.67
48	2.25	25	1.00	10.00	.29	1.67
[2]49	2.75	25	1.00	10.00	.29	1.67
[3]50	2.75	25	1.00	10.00	.29	1.67
[4]51	2.75	25	1.00	10.00	.29	1.67
[5]52	2.75	25	1.00	10.00	.29	1.67
101	3.00	25	1.00	10.00	3.33	0.00
102	2.50	25	1.00	10.00	3.33	.00
103	2.75	35	1.00	10.00	3.33	.00
104	2.75	15	1.00	10.00	3.33	.00
105	2.75	25	3.00	10.00	3.33	.00
106	2.75	25	0.30	10.00	3.33	.00
107	2.75	25	1.00	33.30	3.33	.00
108	2.75	25	1.00	3.33	3.33	.00
109	2.75	25	1.00	10.00	11.10	.00
110	2.75	25	1.00	10.00	1.11	.00
111	3.25	25	1.00	10.00	3.33	.00
112	2.25	25	1.00	10.00	3.33	.00
[1a]113	2.75	25	1.00	10.00	3.33	.00
[1a]114	2.75	25	1.00	10.00	3.33	.00

[1] Midpoint conditions – CH$_2$O tests.
[1a] Midpoint conditions – CH$_3$OH tests.
[2] 0.5 mmol/L Na$_2$SO$_4$ added.
[3] 10.0 mmol/L Na$_2$SO$_4$ added.
[4] 200 mmol/L Na$_2$SO$_4$ added.
[5] 6.0 mmol/L NaCl added.

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$$r_1 = 10^{-6}b_1 C_1{}^{b2} C_4{}^{b3} C_5{}^{b4} \exp(-10^2 b_5((RT)^{-1} - (RT_o)^{-1})$$
$$+ b_6[H^+] + b_7[H^+]^2 + b_{15}C_6 + 10^{-3}b_{16}C_7) \quad (14)$$

$$r_2 = 10^{-6}b_8 C_2{}^{b9} C_4{}^{b10} C_5{}^{b11} \exp(-10^2 b_{12}((RT)^{-1} - (RT_o)^{-1})$$
$$+ b_{13}[H^+] + b_{14}[H^+]^2 + b_{15}C_6 + 10^{-3}b_{16}C_7) \quad (15)$$

$$r_3 = 10^{-6}b_{17} C_3{}^{b18} C_4{}^{b19} C_5{}^{b20} \exp(-10^2 b_{21}((RT)^{-1} - (RT_o)^{-1})$$
$$+ b_{22}[H^+] + b_{23}[H^+]^2 + b_{24}C_6 + 10^{-3}b_{25}C_7) \quad (16)$$

$$r_4 = 10^{-6}b_{26} C_4{}^{b27} C_5{}^{b28} \exp(-10^2 b_{29}((RT)^{-1} - (RT_o)^{-1})$$
$$+ b_{30}[H^+] + b_{31}[H^+]^2 + b_{32}C_6 + 10^{-3}b_{33}C_7$$
$$+ b_{34}C_1 + b_{35}C_2 + b_{36}C_3) \quad (17)$$

The differential equations and initial concentrations are:

$$\frac{dC_1}{dt} = -r_1, \qquad \text{At } t = 0, \ C_1 = C_{10} \quad (18)$$

$$\frac{dC_2}{dt} = r_1 - r_2, \qquad \text{At } t = 0, \ C_2 = C_{20} \quad (19)$$

$$\frac{dC_3}{dt} = r_2 - r_3, \qquad \begin{array}{l} \text{At } t = 0, \ C_3 = C_{30} \quad (20) \\ C_{30} = 0 \text{ for all} \\ \text{experiments} \end{array}$$

$$\frac{dC_4}{dt} = -r_1 - r_2 - r_3 - r_4, \quad \text{At } t = 0, \ C_4 = C_{40} \quad (21)$$

where:

b_j	=	parameter to be estimated by nonlinear regression,
C_i	=	concentration of species i, mmol/L,
C_1	=	methanol,
C_2	=	formaldehyde,
C_3	=	formic acid,
C_4	=	hydrogen peroxide,
C_5	=	ferric chloride,
C_6	=	sodium chloride,
C_7	=	sodium sulfate,
$[H^+]$	=	concentration of hydrogen ion, mmol/L,
t	=	time, seconds,
T	=	temperature, K,
T_o	=	reference temperature, 298.15 K,
R	=	gas constant = 0.008314 kJ/(mol·K)

Reaction rate equations (14), (15), (16), and (17) contain the standard empirical power function relationships for the reactants and the catalyst, the Arrhenius relationship to describe temperature dependence, and an exponential function to describe the effect of hydrogen ion, promoter, and inhibitor concentrations. Scaling factors are included as required by the Marquardt nonlinear regression algorithm to maintain similar orders of magnitude for major parameters.

The reference temperature, T_o, is included to reduce the correlation between parameters b_1 and b_5, b_8 and

b_{12}, b_{17} and b_{21}, and b_{26} and b_{29}. The parameters $10^2 b_5$, $10^2 b_{12}$, $10^2 b_{21}$, and $10^2 b_{29}$ represent the Arrhenius activation energies in kilojoules per mole.

The exponential relationship was chosen to describe the effect of hydrogen ion, promoter, and inhibitor concentrations to avoid negative values. For lack of data, the effects of sodium chloride and sodium sulfate on the oxidation of methanol are assumed to be the same as their effects on the oxidation of formaldehyde, refer to parameters b_{15} and b_{16} in equations (14) and (15).

Although the set of experiments was not designed to estimate inhibition of reactions by the reactants themselves, poor fit of hydrogen peroxide concentrations (without parameters b_{34}, b_{35} and b_{36}) and a review of references [6,7] indicated the need for parameters b_{34}, b_{35} and b_{36}, refer to equation (17). Of the three organic reactants, only methanol has been cited [7, 8] as an inhibitor of the decomposition of hydrogen peroxide.

Parameter Estimation

Values of concentration versus time for the 65 experiments were computed from the initial values and equations (14) through (21) using the IMSL FORTRAN numerical integration subroutine DGEAR [4]. Weighted residuals of the concentrations of hydrogen peroxide, formaldehyde, and formic acid were computed as:

$$res_1 = \frac{C_4 - C_4'}{s_4} \quad (22)$$

$$res_2 = \frac{C_2 - C_2'}{s_2} \quad (23)$$

$$res_3 = \frac{C_3 - C_3'}{s_3} \quad (24)$$

where C_i' is the calculated concentration of species i, and s_i is the estimated analytical accuracy in measuring the concentration of species i. Both Gauss and Marquardt algorithms in SPSS Nonlinear [5] were used to perform the nonlinear regressions.

Thirty-Six-Parameter Model. – Table 6 lists the parameter estimates and standard errors for all 36 parameters in equations (14) through (21). In estimating the standard errors, the total number of independent observations was conservatively evaluated to be 179 (57 experiments times 3 response variables plus 8 experiments times 1 response variable). With 36 estimated parameters, the number of degrees of freedom is 143. Because only one experiment contained sodium chloride, no standard errors are listed

Table 6. – Thirty-six-parameter empirical reaction-rate model parameter estimates and standard errors.

	Reaction							
	Oxidation of methanol		Oxidation of formaldehyde		Oxidation of formic acid		Decomposition of hydrogen peroxide	
Parameter:								
Rate coeff. 10^{-6}	b_1	6.16 (0.12)	b_8	5.84 (0.05)	b_{17}	4.02 (0.10)	b_{26}	9.01 (0.12)
Order of organic reactant	b_2	0.344 (0.020)	b_9	0.560 (0.044)	b_{18}	0.409 (0.058)		
Order of hydrogen peroxide	b_3	0.955 (0.023)	b_{10}	1.17 (0.03)	b_{19}	1.28 (0.03)	b_{27}	1.50 (0.04)
Order of ferric chloride catalyst	b_4	0.899 (0.071)	b_{11}	0.832 (0.077)	b_{20}	0.873 (0.079)	b_{28}	1.19 (0.07)
Activation energy, kJ/mol	$10^2 b_5$	66.6 (4.0)	$10^2 b_{12}$	63.3 (6.8)	$10^2 b_{21}$	57.3 (6.8)	$10^2 b_{29}$	51.6 (7.8)
Exponential coefficients:								
$[H^+]$ L/mmol	b_6	0.384 (0.029)	b_{13}	0.703 (0.032)	b_{22}	0.393 (0.037)	b_{30}	1.34 (0.11)
$[H^+]^2$ $(L/mmol)^2$	b_7	−0.060 (0.013)	b_{14}	−1.131 (0.010)	b_{23}	−0.102 (0.018)	b_{31}	−0.192 (0.029)
$[NaCl]$ L/mmol	$= b_{15}$		b_{15}	0.102 (−)	b_{24}	0.145 (−)	b_{32}	0.119 (−)
$[Na_2SO_4]$ 10^{-3} L/mmol	$= b_{16}$		b_{16}	−6.30 (3.26)	b_{25}	−5.56 (2.91)	b_{33}	−4.43 (9.06)
$[CH_3OH]$ L/mmol							b_{34}	−2.05 (0.06)
$[CH_2O]$ L/mmol							b_{35}	−0.463 (0.137)
$[CH_2O_2]$ L/mmol							b_{36}	−1.48 (0.10)

Note: Values in parentheses are estimated standard errors.

for parameters b_{15}, b_{24}, and b_{32}. The root-mean-square residual for 846 degrees of freedom (including observations from all 5 sampling times for each experiment) is 4.5.

The reaction order estimate for formaldehyde of 0.56 is less than the order of 1 calculated by Dunicz et. al. [9], but not significantly different from the two-thirds value calculated by Satterfield and Case [10]. The reaction order estimates for methanol and formic acid are lower, approximately 0.4

The rates of oxidation of the three organics all appear to be approximately proportional (first-order) to the hydrogen peroxide concentration. For hydrogen peroxide decomposition the reaction-order estimate for hydrogen peroxide is 1.5, which is the theoretical and observed value reported by [11]. The order of the ferric chloride catalyst is approximately 1.0 for all four reactions including the decomposition of hydrogen peroxide as reported by [11] for the ferric ion alone (without chloride).

Sixteen-Parameter Model. – Many of the parameter estimates in table 6 have similar values. To reduce the number of estimated parameters, common parameter values were assumed:

b_2, b_9, b_{18}:	Order of organic reactants
b_3, b_{10}, b_{19}:	Order of hydrogen peroxide in reactions 1, 2, and 3
b_4, b_{11}, b_{20}:	Order of ferric chloride catalyst in reactions 1, 2, and 3
b_5, b_{12}, b_{21}:	Activation energy in reactions 1, 2, and 3
b_6, b_{13}, b_{22}:	[H$^+$] coefficient in reactions 1, 2, and 3
b_7, b_{14}, b_{23}:	[H$^+$]^2 coefficient in reactions 1, 2, and 3
b_{15}, b_{24}, b_{32}:	[NaCl] coefficient in reactions 1, 2, 3, and 4
b_{16}, b_{25}, b_{33}:	[Na$_2$SO$_4$] coefficient in reactions 1, 2, 3, and 4
b_{34}, b_{35}, b_{36}:	Organic reactant coefficient in reaction 4

In addition, the order of hydrogen peroxide was assumed to be 1.00 in reactions 1, 2, and 3 and 1.50 (the theoretical value) in reaction 4. These assumptions reduce the number of estimated parameters from 36 to 16 and resulted in an increase in the sum of squares of the residuals of only 12 percent. Regression results with the common parameter estimates are listed in table 7. For estimating the standard errors with 16 estimated parameters, the number of degrees of freedom is 163. The root-mean-square residual for all observations (d.f. = 866) is 4.7.

Figures 23(a), (c), and (d) show the concentrations of organic reactants and hydrogen peroxide as predicted by the 16-parameter model. At the midpoint conditions, the curve fit is good for formaldehyde and formic acid concentrations, see figure 23(a). The addition of sodium sulfate at midpoint conditions severely reduces the rate of reactions, see figure 23(c). For high initial concentrations of hydrogen peroxide and formaldehyde, figure 23(d), the curve fit is less accurate. The poor fit to hydrogen peroxide data may be due to an error in the initial hydrogen peroxide concentration.

Discussion

Comparing the rate coefficients b_1, b_8, and b_9 of the three organic oxidation reactions (see table 7), the rate of oxidation of formaldehyde is approximately twice the oxidation rates for methanol and formic acid. The rate of decomposition of hydrogen peroxide at the beginning of the midpoint experimental conditions (see table 4) is approximately equal to the rate of oxidation of formaldehyde.

Defining the hydrogen peroxide efficiency, η, as the rate of hydrogen peroxide oxidation of organic reactants divided by the total rate of hydrogen peroxide disappearance, then:

$$\eta = \frac{r_1 + r_2 + r_3}{r_1 + r_2 + r_3 + r_4}$$

The efficiency, η, is not constant but decreases with reaction time as the oxidation rates r_1, r_2, and r_3 (which vary with organic concentration) decline, see figures 23(a) and (b). At the midpoint experimental conditions, η falls from an initial value of 0.62 to an estimated 0.41 after 200 minutes.

The 16-parameter model estimates a common order of 0.5 for the organic concentrations in the oxidation reactions 1, 2, and 3. Compared with the first-order initially assumed, this 0.5-order extrapolates higher reaction rates at low concentrations (e.g. 1 mg/L) of formaldehyde and formic acid.

For the ferric chloride catalyst, the 16-parameter model estimates a common order of 0.8 in reactions 1, 2, and 3, significantly less than the estimated order of 1.2 for decomposition reaction 4. Thus, the optimum concentration of ferric chloride may be bracketed by low catalyst concentrations where oxidation reactions 1, 2, and 3 may proceed too slowly and by high catalyst concentrations where the undesirable decomposition reaction 4 is favored.

All four reaction rates exhibit a maximum as a function of hydrogen ion concentration. Figure 24 shows

the effect of pH on the reaction rates as estimated by the 36-parameter model. The hydrogen ion concentrations and pH values corresponding to maximum reaction rates are:

Model	Reaction	$[H^+]$ max., mmol/L	pH max.
36-parameter	1	3.19	2.50
	2	2.69	2.57
	3	1.93	2.72
	4	3.53	2.45
16-parameter	1,2,3	2.54	2.60
	4	3.42	2.47

The pH dependence of the reaction rates indicate that within the range of the experimental conditions, the optimum pH for maximizing the organic oxidation rates and minimizing the rate of decomposition of hydrogen peroxide is above 2.7 and probably below 3.2. This optimum pH range is consistent with the recommended pH range of 2.75 to 3.00 in the section entitled "Reaction pH Dependence." High reactor costs and low hydrogen peroxide costs would favor an optimum pH of approximately 2.75. High peroxide costs and low reactor costs would favor an optimum pH of 3.0 to 3.2.

The organic reactants significantly inhibit the decomposition of hydrogen peroxide. An organic concentration of 2.0 mmol/L (initial organic concentration at the experimental midpoint formaldehyde level of 50 mg/L) reduces the decomposition rate by approximately 83 percent (with the estimated value of b_{35} in table 7, $1 - \exp[-0.881 \times 2.0] = 0.83$) compared with the rate in the absence of organics. This reduction is equivalent to reducing the ferric chloride catalyst concentration by a factor of 4 or reducing the temperature by 29 °C. The strong inhibition indicates that only a small amount of hydrogen peroxide would be lost through decomposition by adding all of the hydrogen peroxide at one time as opposed to adding it over the entire oxidation period. This agrees with the observations made earlier in the discussion of the phase II pilot-scale test results. Competitive or other inhibitive effects of the organic reactants for reactions 1, 2, and 3 could not be discerned from this set of experiments.

Sodium sulfate inhibits both organic oxidation and hydrogen peroxide decomposition reaction rates. A concentration of 200 mmol/L, corresponding to an air-oxidized 2.5-percent sodium bisulfite solution, reduces the reaction rates by 70 percent (with the estimated value of b_{16} in table 7, $1 - \exp[-0.00607 \times 200] = 0.70$) compared with the rates in the absence of sodium sulfate.

Sodium chloride appears to promote the reaction rates. Based on one experiment (test 52), 6 mmol/L

(351 mg/L) of sodium chloride doubled the reaction rates (with the estimated value of b_{15} in table 7, exp $[0.109 \times 6.0] = 1.9$). For organic oxidations, this increase is equivalent to that resulting from increasing the ferric chloride catalyst concentration from 1.0 to 2.4 mmol/L. Thus, if chloride ion is the promoting ion [12], it appears that approximately 70 percent of the promoting effect of the ferric chloride catalyst between the midpoint and high experimental catalyst concentrations is from the chloride anion. Because high ferric chloride catalyst concentrations favor the hydrogen peroxide decomposition reaction, sodium chloride plus a low ferric chloride concentration may serve as a better catalytic reagent provided high sodium chloride concentrations do not favor hydrogen peroxide decomposition.

The Arrhenius activation energies range from 44 to 67 kJ/mol (11 to 16 kcal/mol) for the four reactions. These activation energies correspond to rate increases of 6 to 10 percent per °C, or factors of 1.8 to 2.5 for a 10 °C rise in temperature (20 to 30 °C).

Figures 25 and 26 present extrapolations of the 16-parameter model outside the range of the experimental conditions used to estimate the empirical parameters. This was done to facilitate comparisons of the model with adiabatic test data (fig. 25) and to estimate total reaction times required for the oxidation of formaldehyde solutions using high initial concentrations of hydrogen peroxide (fig. 26). The reader should be cautioned that the isothermal tests and resulting model were designed to evaluate the oxidation at low concentrations[2]; i.e., near the completion of the reaction. Consequently, extrapolations of the model to higher concentrations may be of questionable accuracy.

Figure 25 shows the 16-parameter model predictions for the adiabatic (phase I and II) midpoint test conditions (table 1). Figure 25(a) presents the comparison for formaldehyde and formate, and figure 25(b) gives the comparison for hydrogen peroxide. As was discussed earlier in the report, the phase I bench-scale midpoint oxidation appears to proceed about 20 percent faster than the phase II pilot-scale oxidation (based on the disappearance of formate). On figure 25(a), the 16-parameter model predicts an even faster oxidation during the first 75 to 90 minutes of the reaction. However, after 90 minutes the adiabatic tests show formate quickly disappearing to below the ion chromatograph detection limit of about 3 mg/L (0.065 mmol/L); whereas, the model predicts

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[2] In the isothermal experiments, the maximum hydrogen peroxide and ferric chloride concentrations were 33.3 and 3.0 mmolar, respectively. The range of formaldehyde and formic acid measurements was approximately 0.1 to 17 mmolar.

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Table 7. — Sixteen-parameter empirical reaction-rate model parameter estimates and standard errors.

| | Reaction | | | |
	Oxidation of methanol	Oxidation of formaldehyde	Oxidation of formic acid	Decomposition of hydrogen peroxide
Parameter:				
Rate coeff. 10^{-6}	b_1 4.80 (0.40)	b_8 10.72 (0.51)	b_{17} 5.87 (0.29)	b_{26} 10.56 (1.00)
Order of organic reactant	$b_2 = b_9$	b_9 0.529 (0.023)	$b_{18} = b_9$	
Order of hydrogen peroxide	b_3 1.00	b_{10} 1.00	b_{19} 1.00	b_{27} 1.50
Order of ferric chloride catalyst	$b_4 = b_{11}$	b_{11} 0.805 (0.093)	$b_{20} = b_{11}$	b_{28} 1.24 (0.16)
Activation energy, kJ/mol	$10^2 b_5$ 66.6 (4.0)	$10^2 b_{12}$ 63.3 (6.8)	$10^2 b_{21}$ 57.3 (6.8)	$10^2 b_{29}$ 51.6 (7.8)
Exponential coefficients:				
$[H^+]$ L/mmol	$b_6 = b_{13}$	b_{13} 0.479 (0.019)	$b_{22} = b_{13}$	b_{30} 1.20 (0.10)
$[H^+]^2$ $(L/mmol)^2$	$b_7 = b_{14}$	b_{14} −0.094 (0.012)	$b_{23} = b_{14}$	b_{31} −0.175 (0.037)
$[NaCl]$ L/mmol	$= b_{15}$	b_{15} 0.109 (0.076)	$b_{24} = b_{15}$	$b_{32} = b_{15}$
$[Na_2SO_4]$ 10^{-3} L/mmol	$= b_{16}$	b_{16} −6.07 (2.43)	$b_{25} = b_{16}$	$b_{33} = b_{16}$
$[CH_3OH]$ L/mmol				$b_{34} = b_{35}$
$[CH_2O]$ L/mmol				b_{35} 0.881 (0.107)
$[CH_2O_2]$ L/mmol				$b_{36} = b_{35}$

Notes: Values in parentheses are estimated standard errors.
Order of hydrogen peroxide values were fixed before regression.

a much slower decay of formate, requiring well over 200 minutes to reach the IC detection limit.

Figure 25(b) shows a close comparison between the model prediction for hydrogen peroxide and the pilot-scale data. Also shown is a model parameter referred to as the H_2O_2 (hydrogen peroxide) efficiency. This parameter graphically reflects the ability of organics (CH_2O and CH_2O_2) to inhibit the decomposition of hydrogen peroxide to oxygen and water. As shown, the H_2O_2 efficiency remains at a high value, near 100 percent, until the formaldehyde disappears and formate is on a steep decline (approx. 35 minutes reaction time), at which time the decomposition reaction accelerates.

Figure 26 summarizes the total reaction times required to oxidize formaldehyde storage solution to a formic acid concentration of 0.333 and 0.033 mmol/L (molar concentrations equivalent to 10 and 1 mg/L formaldehyde, respectively) as predicted by the 16-parameter model. The predicted curves correspond to pH = 2.75, temperature = 25 °C, and the absence of promoting and inhibiting inorganic solutes such as sodium chloride and sodium sulfate. Curves are presented for three initial hydrogen peroxide concentrations: 50, 100, and 200 mmol/L; and two catalyst concentrations: 1.00 mmol/L Fe^{+3} (isothermal midpoint) and 3.33 mmol/L Fe^{+3} (adiabatic midpoint). The total reaction times on figure 26 may be multiplied by 3 for predicting operation at 15 °C, and by 0.5 for operation at 35 °C.

Of the 12 reaction time curves on figure 26, those on figure 26(c) for initial hydrogen peroxide concentrations of 50 and 100 mmol/L correspond most closely to the range of experimental conditions. All figure 26 curves, however, may be used for developing preliminary process designs and selecting the optimum (least cost) concentrations of hydrogen peroxide and ferric chloride for expected ranges of formaldehyde concentration and temperature. If the projected optimum concentrations of hydrogen peroxide and ferric chloride are not within the ranges of the phase II isothermal experiments, then additional experiments should be conducted to measure and verify the rates of reaction in the region of the optimum concentrations.

BISULFITE-REGENERATED ION EXCHANGE TESTING

A procedure involving anion exchange was proposed as a method of concentrating low levels of residual formaldehyde to be flushed from the RO control blocks at the Yuma Desalting Plant [13]. This would allow the reuse of effluent from the exchange process for additional control block flushing, which would result in a considerable savings of water.

The procedure is not a true ion exchange process because formaldehyde reacts with bisulfite already absorbed into the anion exchange resin rather than being exchanged itself. Initially, the resin is placed in the bisulfite ion form:

$$R-Cl + NaHSO_3 \longrightarrow R-HSO_3 + NaCl$$
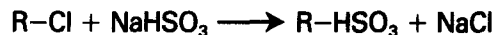
Subsequently, the solution containing formaldehyde is passed through the resin enabling the formation of an adduct of formaldehyde and bisulfite to occur:

$$R-HSO_3 + CH_2O \longrightarrow R-HSO_3 \cdot CH_2O$$

It is this step that would be used to remove formaldehyde from the flushing water. When the resin is exhausted, regeneration is necessary by passing a solution of bisulfite ion through the bed:

$$R-HSO_3 \cdot CH_2O + NaHSO_3 \longrightarrow R-HSO_3 + NaHSO_3 + NaHSO_3 \cdot CH_2O$$
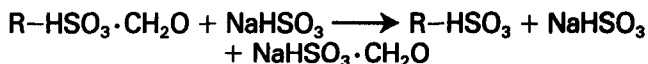
Thus, the eluate from the regeneration contains $NaHSO_3$ and concentrated CH_2O that can be directed to the oxidation tank for final disposal.

An experimental approach was developed to investigate the potential of this method to concentrate formaldehyde. Two methods of testing were used: equilibrium and dynamic. Equilibrium testing is beneficial in providing information about the behavior of the system when in different environments, i.e. different formaldehyde concentrations, flow conditions, pH, and background TDS. Dynamic testing provides concentration histories that furnish both breakthrough information and formaldehyde capacity data. Both methods were valuable tools in determining the effectiveness of this exchange process to remove formaldehyde.

Experimental Apparatus and Procedures

Equilibrium Tests. – Equilibrium tests were used to supply information regarding system behavior under different operating conditions. These included varying formaldehyde feed concentration, flow rate, total volume of throughput, pH, and the amount of rinse water used between exhaustion and regeneration. Rinse water is important because of the effect it can have on the equilibrium established during exhaustion between formaldehyde and bisulfite. In addition, tests were performed using both deionized water and synthesized Yuma service water to determine the effect of chloride and sulfate ions on the system (see the analysis of Yuma service water in table 2). This series of tests provided an accurate measurement of the amount of formaldehyde that reacts with the bisulfite on the resin under specific conditions, the so-called "formaldehyde capacity."

The test apparatus used for these experiments included glass burets, each of which contained 10 mL of Amberlite IRA-402 anion exchange resin. This resin, manufactured by Rohm and Haas, is a strongly basic gelular anion exchange resin with a styrene divinylbenzene copolymer matrix. The resin was supported by a layer of glass wool that prevented the resin from passing out the bottom of the buret. Test solutions were supplied to the burets from elevated feed tanks. Flow rates were adjusted and set from the buret stopcock.

The procedures involved initially placing the resin in the OH⁻ form by passing 500 mL of 4-percent NaOH through the bed at approximately 9 mL/min. Regeneration with 500 mL of 10-percent $NaHSO_3$ then put the resin in the bisulfite form (flow rate approximately 11 mL/min). Finally, a 40-mL water rinse was performed to flush excess bisulfite solution from the bed pore volume.

An experimental design matrix for the equilibrium tests, including the operating conditions for each buret, is shown in table 8. The matrix outlines the independent variables investigated: CH_2O influent concentration, the use of deionized versus Yuma service water, length of water rinse, pH, flow rates, and total volume throughput. In each test, influent and effluent samples were collected for comparison just before the depletion of the feed volume to ensure that equilibrium conditions had been met. Another water rinse followed the exhaustion step to remove formaldehyde from the pore volume before regeneration.

A two-step regeneration was conducted to ensure complete removal of formaldehyde. Each involved injecting 500 mL of 10-percent $NaHSO_3$ into the bed at a flow rate of about 2 mL/min. The entire effluent volume of each regeneration was collected separately, and then mixed well to provide a homogeneous solution. These solutions were then analyzed for total formaldehyde content, thus providing the "formaldehyde capacity" value. The formaldehyde content was analyzed using the ion chromatographic method described in appendix E.

Dynamic Tests. – Dynamic tests were conducted so that the behavior of the pertinent species, CH_2O, HSO_3^- and Cl^-, might be examined throughout the ion exchange cycle. These tests provided breakthrough information and formaldehyde capacity data under different operating conditions.

A schematic of the experimental apparatus, which consists of an ion exchange column and required accessories, is shown on figure 27. The column was constructed of heat-resistant glass with Teflon and polypropylene end fittings. It was about 2 m long

with an inside diameter of 25 mm. Surrounding the column was a glass water jacket that provided a constant temperature environment for the process. A temperature-controlled water bath provided the heating and cooling to the jacket and contained tubing coils for the influent streams. Variable-speed, positive-displacement roller tubing pumps supplied the exhaustion and regeneration streams to the column, and the flows were monitored by rotameters and regular bucket-and-stopwatch measurements. The exhaustion and regeneration tanks were polyvinyl chloride and had capacities of 208 and 57 L, respectively. Pressure gauges and glass thermometers provided pressure and temperature readings.

The column contained 500 mL of the Amberlite IRA-402 resin manufactured by Rohm and Haas, identical to the resin tested in the equilibrium work. The bed was supported by a mesh that prevented loss of resin from the column.

The procedures involved with the dynamic tests were similar to those for the equilibrium work except that the effluent concentration history was characterized. Initially, the resin was placed in the OH⁻ form by injecting 10 L of 4-percent NaOH into the column at a rate of 25 mL/min. The resin was converted to the bisulfite form with 5 L of 10-percent $NaHSO_3$ also at a flow rate of 25 mL/min. A water rinse was then provided to flush the excess $NaHSO_3$ from the pore volume. The prescribed formaldehyde solution was then fed into the bed while effluent samples were collected from the bottom of the column at intermittent times. These samples were then analyzed, using the ion chromatograph, to provide a concentration history of the pertinent ions. The analyses were complicated by having to predict, in advance, an appropriate bisulfide concentration for each sample.

Results and Discussion

Equilibrium Tests. – The agreement between the concentrations of influent and effluent pairs confirms that equilibrium between solution and resin had been achieved. When the initial regeneration samples were analyzed, formaldehyde was found only in the deionized water test, column 1. The other tests (columns 2 through 6) used simulated Yuma service water in the exhaustion step. This water contains a considerable amount of chloride and sulfate ions, 157.9 mg/L and 10.2 mg/L, respectively (table 2). The regeneration samples from columns 2 through 6 contained large chloride concentrations but no detectable formaldehyde. This indicates that chloride ions had replaced bisulfite ions on the resin during exhaustion. Without bisulfite retention on the resin, no net formaldehyde removal was possible under the experimental conditions. However, the dynamic tests described below did show formaldehyde removal.

Table 8. — Experimental design for ion exchange equilbrium testing.

| Col-
umn
No. | CH₂O concentration | | | | Back-
ground
TDS | Rinse
duration | pH | Flow rate,
mL/min | Total
volume,
L |
| | Influent | | Effluent | | | | | | |
	mg/L	meq/L	mg/L	meq/L					
1	53.1	1.77	49.5	1.65	DI	Normal	7	6.3	40
2	44.4	1.48	40.8	1.36	YSW	Normal	7	6.7	40
3	6.9	0.23	*	*	YSW	Normal	7	3.4	190
4	243.9	8.13	243.9	8.13	YSW	Normal	7	5.7	8
5	44.4	1.48	44.4	1.48	YSW	Long	7	6.4	40
6	44.4	1.48	42.3	1.41	YSW	Normal	10	5.9	40

*   Unmeasured.
DI   Deionized water.
YSW   Yuma service water (synthesized): 300 mg/L (see table 2).

There was quantitative removal of formaldehyde from column 1, which used deionized water without added salt for the exhaustion feed water. The regeneration sample contained 11.25 meq of formaldehyde (1.12 meq/mL resin). This is an adequate removal considering that Rohm and Haas indicates a 1.25-meq/mL resin total anion exchange capacity for IRA-402 anion exchange resin. Thus, practical formaldehyde removal is possible provided that effects of anions in the feedwater can be overcome.

Dynamic Tests. — Two dynamic tests were designed based on the equilibrium test results. The purposes of these tests were (1) to further support the conclusion from the equilibrium work that chloride ions were indeed replacing bisulfite ions on the resin, (2) to illustrate when this exchange was occurring during the exhaustion step, and (3) to provide data on the feasibility of the practical application of the process.

The exhaustion of the resin in the bisulfite form was conducted using the following two sets of test conditions:

| | Water Composition
(mg/L) (meq/L) | | | Flow
rate,
mL/min | Temp.,
°C |
	CH₂O	Cl⁻	SO₄⁻²		
Test 1	501 /16.7	1579/44.5	102 /2.13	200	25
Test 2	48.9/1.63	157.9/4.45	10.2/0.21	300	25

Figure 28 depicts the concentration history or profile of formaldehyde and chloride ions throughout exhaustion for dynamic test 1. This history represents the effluent concentrations of the respective ions as collected from the bottom of the column. A 10-fold concentration increase over equilibrium test conditions was used in dynamic test 1 to shorten the time required to reach equilibrium such that the test could be conducted in a reasonable amount of time. Figure 28 indicates that chloride ions are indeed taken up by the resin and chloride breakthrough occurs at

about 15 bed volumes, after which there is no further net removal of formaldehyde. Since a bed volume represents 500 mL, 15 bed volumes is equivalent to 7.5 L of solution passing through the column. Formaldehyde appears in the effluent solution after 10 bed volumes, and the peak of its breakthrough occurs at approximately 22 bed volumes. This early breakthrough shows how chloride was preferentially absorbed relative to bisulfite.

Gabrielson and Samuelson [13] indicated some problems with quantitative formaldehyde removal. Two possible explanations are that the formaldehyde-bisulfite bond breaks up with continued water throughput or that the HSO_3^-·CH_2O absorbed at the top of the anion exchanger is displaced by Cl^- and not reabsorbed below because the exchange sites are already occupied by HSO_3^-. Either or both of these equilibria could cause the observed leakage.

Figure 29 and table 9 present the concentration profile (formaldehyde and chloride breakthrough) resulting from dynamic test 2 and associated tabulated data, respectively. The feed concentration used corresponds to that tested in the equilibrium studies. Leakage of formaldehyde appeared gradually, at about 60 bed volumes, as chloride ions displaced bisulfite ions (adduct of formaldehyde and bisulfite) on the resin. Figure 30 shows the accumulated average leakage for both ions.

The discrepancy between the breakthrough point of the two dynamic tests (10 L throughput for test 1 at a 10-fold concentration compared with 60 L throughput for test 2) results from, as previously discussed, the equilibrium of the adduct compound HSO_3^-·CH_2O and/or the equilibrium and column dynamics of HSO_3^- on the anion exchange resin.

Though the bisulfite was preferentially stripped from the resin in exchange for chloride ions, the process removed considerable formaldehyde from the feed stream before the bisulfite ions on the resin had been

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Table 9. – Formaldehyde and chloride concentration versus bed volumes for dynamic test 2.

| | Effluent Concentration | | | | Accumulated Average Leakage | | | | Resin Capacity, eq/L of Resin | |
| | mg/L | | meq/L | | mg/L | | meq/L | | | |
Bed Volume	CH_2O	Cl^-	CH_2O	Cl^-	CH_2O	Cl^-	CH_2O	Cl^-	CH_2O	Cl^-
INFLUENT:	48.9	157.9	1.63	4.45	–	–	–	–	–	–
0.0	0.0	0.0	0.00	0.00	0.0	0.0	0.00	0.00	0.00	0.00
12.0	.1	.0	.00	.00	.1	.0	.00	.00	.02	.05
36.2	.5	.0	.02	.00	.2	.0	.01	.00	.06	.16
60.1	1.0	.0	.03	.00	.4	.0	.01	.00	.10	.27
78.1	1.8	.0	.06	.00	.7	.0	.02	.00	.13	.35
96.4	2.8	.0	.09	.00	1.0	.0	.03	.00	.15	.43
108.3	3.9	.0	.13	.00	1.2	.0	.04	.00	.17	.48
120.2	7.7	.0	.26	.00	1.7	.0	.06	.00	.19	.53
132.1	11.2	.0	.37	.00	2.4	.0	.08	.00	.20	.59
141.1	16.0	.0	.53	.00	3.1	.0	.10	.00	.22	.63
150.2	22.2	.0	.74	.00	4.1	.0	.14	.00	.22	.67
159.5	30.0	.0	1.00	.00	5.4	.0	.18	.00	.23	.71
174.4	40.0	.0	1.33	.00	7.9	.0	.26	.00	.24	.78
183.3	50.0	.1	1.67	.00	9.7	.0	.32	.00	.24	.82
192.1	60.0	1.0	2.00	.03	11.8	.0	.39	.00	.24	.85
201.0	78.0	2.0	2.60	.06	14.3	.1	.48	.00	.23	.89
210.0	96.0	3.0	3.20	.08	17.4	.2	.58	.01	.22	.93
219.1	106.0	7.0	3.53	.20	20.9	.4	.70	.01	.20	.97
228.0	115.8	12.0	3.86	.34	24.4	.8	.81	.02	.19	1.01
237.1	120.0	21.0	4.00	.59	28.0	1.4	.93	.04	.17	1.05
246.2	125.0	26.9	4.17	.76	31.5	2.2	1.05	.06	.14	1.08
255.5	120.8	37.5	4.03	1.06	34.8	3.3	1.16	.09	.12	1.11

exhausted. This can be seen both in the data of table 9 and graphically on figure 31. This figure presents the formaldehyde capacity of the resin as a function of the number of bed volumes passed through the bed. The maximum formaldehyde capacity of 0.24 eq/L occurs at approximately 183 bed volumes of throughput. Compared with the 1.25-eq/L total capacity of the resin, as reported by Rohm and Haas [14], less than 20 percent of the available resin was used for formaldehyde removal. However, the total capacity is virtually never achieved in a practical ion exchange process using strong base anion exchange resins because of the large excess of regenerant that would be required. Another consequence of the preference of the resin for chloride over sulfite is that some leakage of formaldehyde begins early in the exhaustion step. Exhaustion can be concluded at an early breakthrough volume to yield a less concentrated effluent stream, but only at the expense of a relatively inefficient use of the available resin.

CONCLUSIONS

1. A comparison of the bench-scale (0.25-L solution volume) and pilot-scale (106.6-L solution volume)

adiabatic midpoint test results indicated a 20-percent slower reaction in the larger reactor.

2. A background salinity of 300 mg/L (synthesized Yuma service water) slowed the reaction by an estimated 10 to 15 percent, compared with tests run with deionized water. A background salinity of 3000 mg/L (10 times the concentration of Yuma service water) slowed the reaction by 60 to 75 percent.

3. Varying the mixing input power for the reaction over a range of 0.0005 to 0.05 watts per liter had virtually no effect on the rate of oxidation. This further verifies the assumption of small diffusional resistance made in an earlier chemical similitude analysis for scale-up.

4. Adding all the hydrogen peroxide at the beginning of the oxidation (batch addition) results in a faster initial reaction rate, but no higher consumption of hydrogen peroxide than for metered addition.

5. During normal operation at or near the optimum pH for the reaction, there will be no sludge with which to contend. However, consideration might be given to increasing the pH at the conclusion of the reaction

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to precipitate iron before final disposal of the solution.

6. The empirical reaction rate model presented in this report can be used at the Yuma Desalting Plant to predict and optimize the hydrogen peroxide oxidation of formaldehyde storage solutions to carbon dioxide and water in the presence of ferric chloride (50 to 500 mg/L), sodium chloride (0 to 400 mg/L), and sodium sulfate (0 to 30 000 mg/L); in the pH range of 2.2 to 3.3; and in the temperature range of 15 to 35 °C. An accurate description of the inhibiting effect of the organic solutes, i.e. methanol, formaldehyde, and formic acid, however, requires further experiments and modeling.

7. Observed rates of oxidation of the organic solutes are proportional to $[CH_3OH]^{0.3}$, $[CH_2O]^{0.6}$, $[CH_2O_2]^{0.4}$, $[H_2O_2]^{1.0 \text{ to } 1.3}$, and $[FeCl_3]^{0.8 \text{ to } 0.9}$. The observed rate of decomposition of hydrogen peroxide is proportional to $[H_2O_2]^{1.5}$ and $[FeCl_3]^{1.2}$.

8. Based on observations made during isothermal testing, maximum reaction rates occur in the pH range of 2.4 to 2.7. The low pH favors the decomposition of hydrogen peroxide, and the high pH favors the oxidation of the organic solutes.

9. The organic solutes significantly inhibit the undesirable decomposition of hydrogen peroxide. A concentration of 50 mg/L formaldehyde and 10 mg/L methanol reduces the decomposition rate by approximately 90 percent.

10. Sodium sulfate inhibits all reactions. A 2.8-percent solution reduces the reaction rates by approximately 70 percent.

11. Sodium chloride promotes all reactions. It appears that 70 percent of the catalytic action of ferric chloride may be from the chloride anion.

12. The activation energies range from 44 to 67 kJ/mol for the four reactions. This corresponds to rate increases of 6 to 10 percent per °C, or a factor of 1.8 to 2.5 increase for a 10 °C rise in temperature (20 to 30 °C).

13. During the ion exchange testing, in which synthesized Yuma service water was used to prepare the formaldehyde feed solutions, chloride was found to be preferentially absorbed by the resin relative to bisulfite. As a result, the maximum formaldehyde capacity of the resin was limited to 0.239 eq/L, less than 20 percent of the 1.25 eq/L total exchange capacity reported by the manufacturer.

14. Despite unfavorable equilibria in the presence of chloride, further study may help develop a practical ion exchange process for concentrating low levels of

residual formaldehyde from RO control blocks. Because of the infrequent use of the process, the economics will be much different than would normally be the case for ion exchange; i.e., regenerant costs probably will not be as significant.

15. The ion exchange process gives potential for recycling formaldehyde as a biocide; however, the feasibility of doing this has not been addressed and would have to be part of a broader engineering analyses including related processes.

16. Although an analysis of alternative construction materials was beyond the scope of this study, the Dow 411 vinyl ester resin used for the fabrication of the reaction tank was determined to be adequate.

RECOMMENDATIONS

1. The curves on figure 26 may be used for developing preliminary process designs and selecting the optimum (least-cost) concentrations of hydrogen peroxide and ferric chloride for expected ranges of formaldehyde concentration and temperature. If the projected optimum concentrations of hydrogen peroxide and ferric chloride are not within the ranges of the phase II isothermal experiments, then additional experiments should be conducted to measure and verify the rates of reaction in the region of the optimum concentrations.

2. The feasibility, design, and selection of the ion exchange process, if used, should be done in conjunction with the RO flushing and oxidation processes. They should be considered integrally to determine overall optimum economics and operability of formaldehyde disposal.

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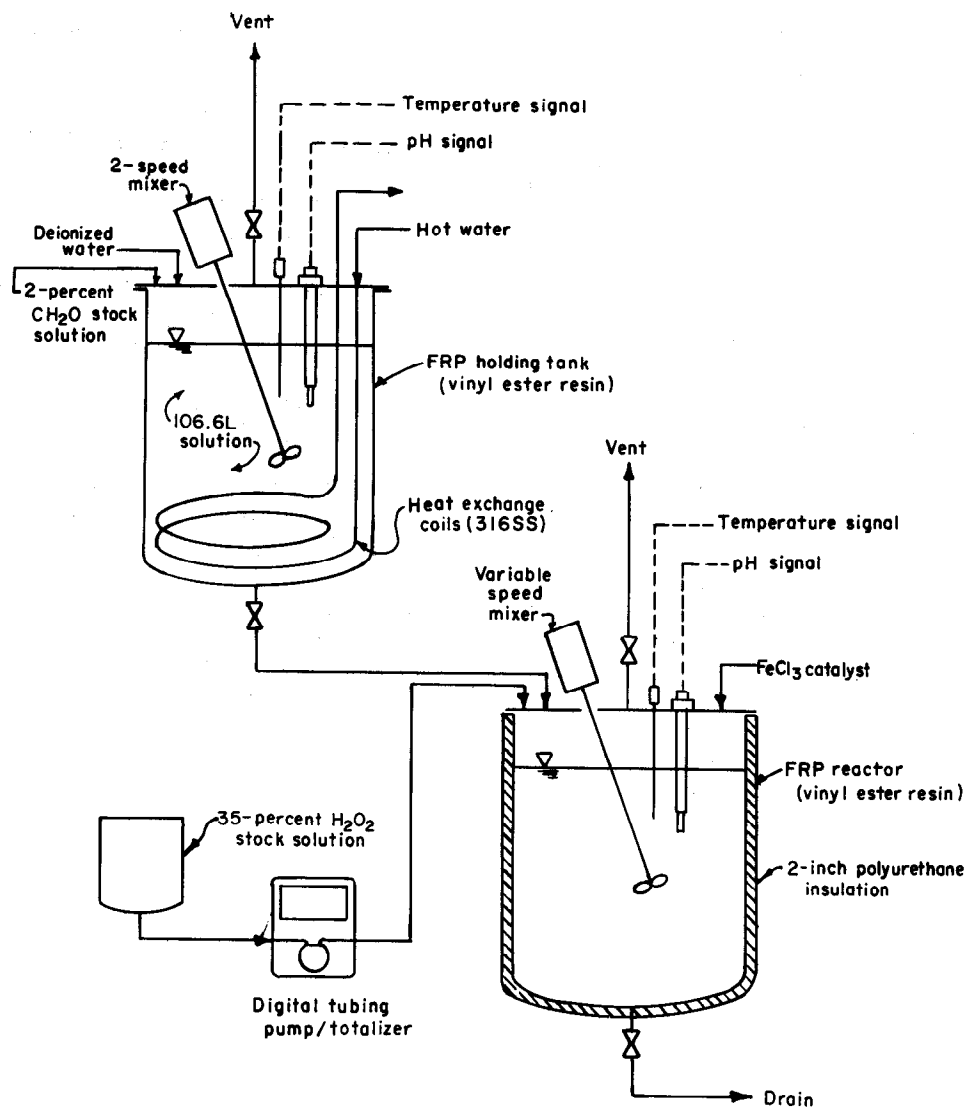
Figure 1. – Pilot plant equipment and instrumentation diagram.
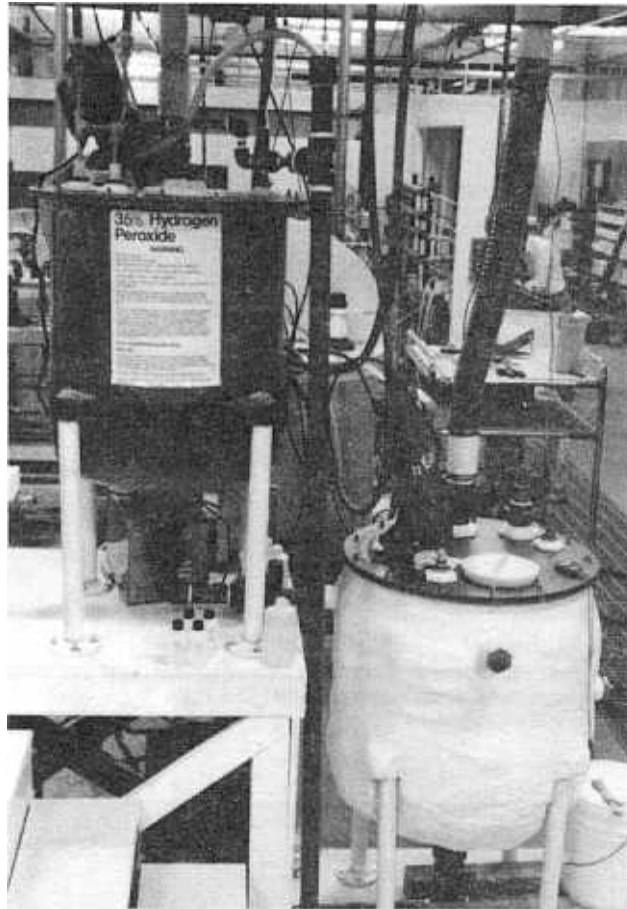
* Figure 2. – Pilot plant including holding tank on the left and
reactor on the right. P801-D-81362
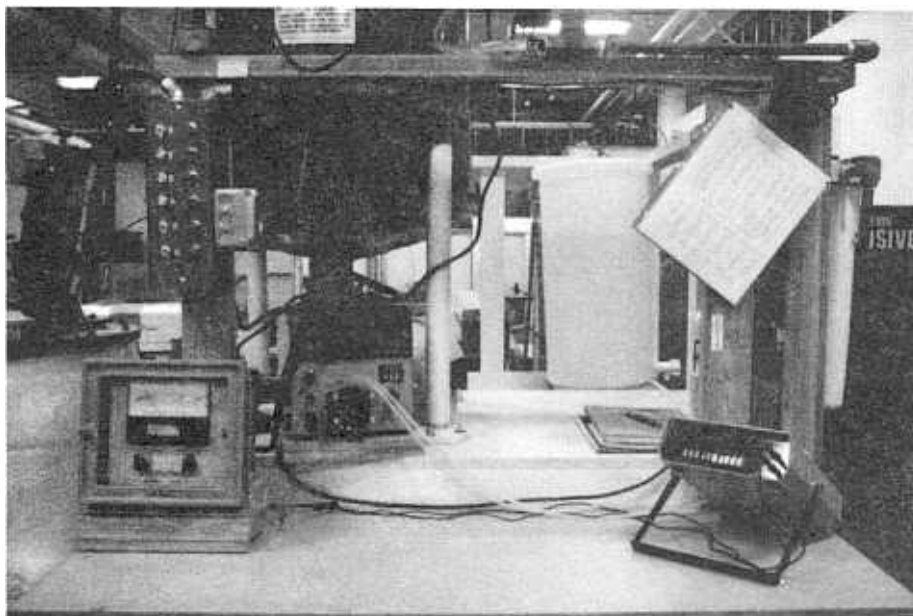
Figure 3. – Pilot plant controls and instrumentation. P801-D-81363

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Figure 4. – Top view of holding tank showing Lightnin mixer, heat exchanger tubing, vent, temperature probe, and access cover. P801-D-81364
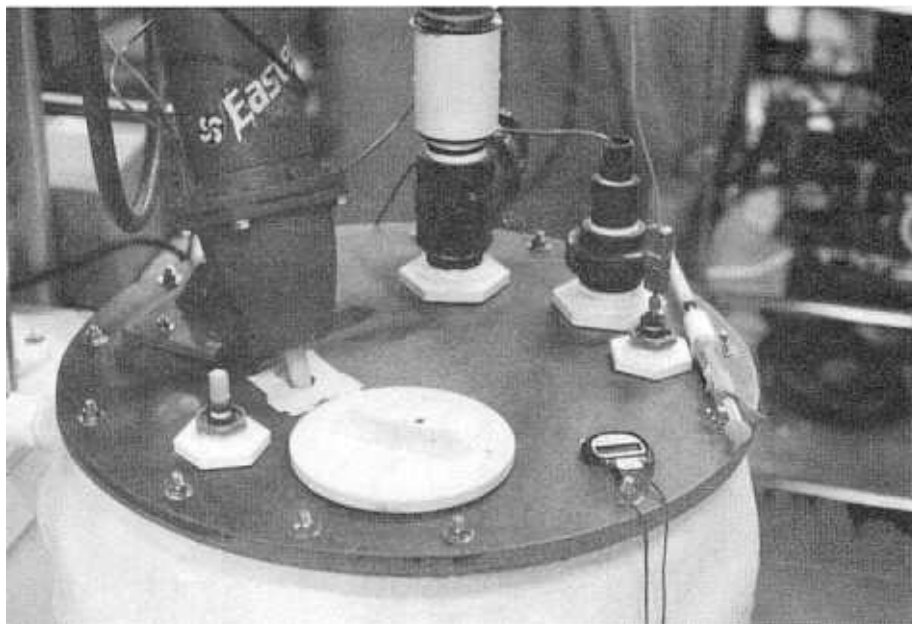
Figure 5. – Top view of insulated reactor showing Eastern variable speed mixer, vent, pH and temperature probes, hydrogen peroxide feed port (lower left), and access cover. P801-D-81365

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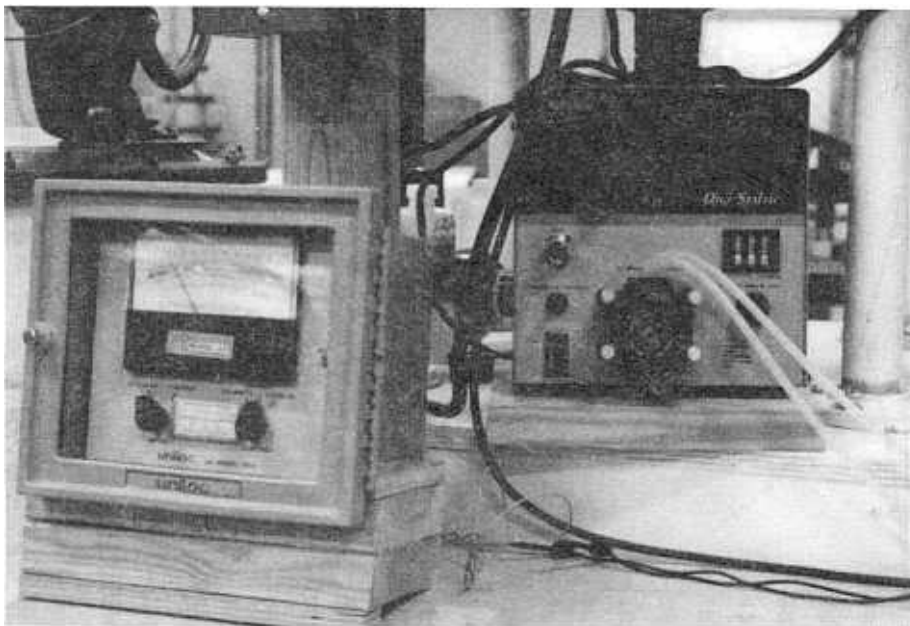
Figure 6. — Uniloc pH analyzer and Masterflex digital flow drive used for metering hydrogen peroxide to the reactor.   P801-D-81366

Figure 7. — Hewlett Packard data acquisition system and Compaq Portable 286 computer used to collect and record pH and temperature data.   P801-D-81367

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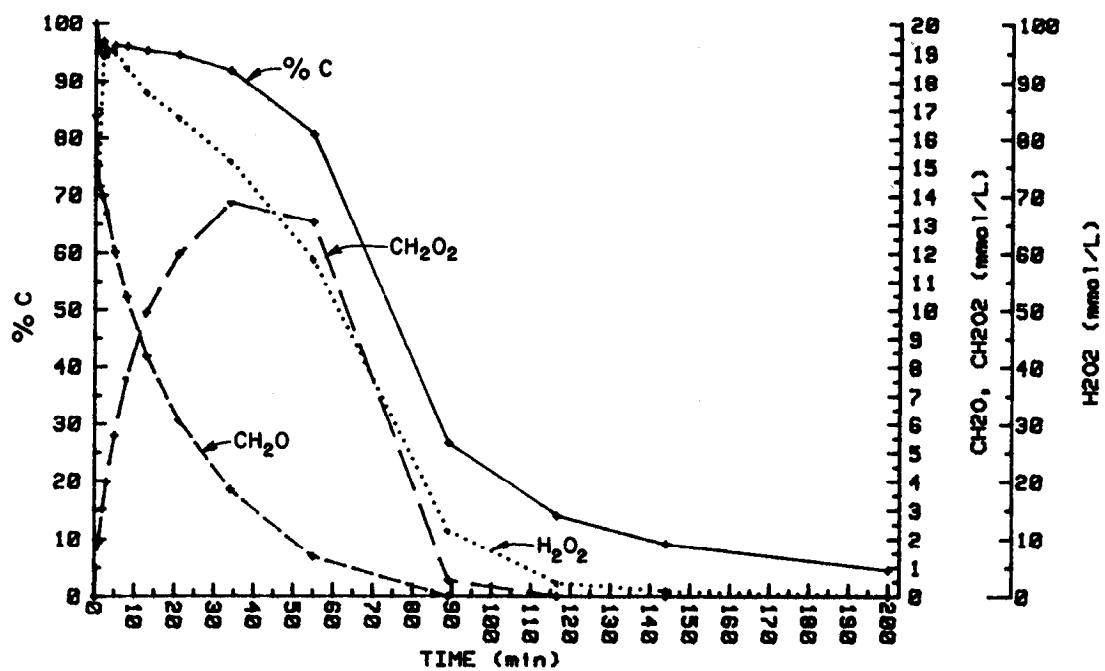
Figure 8. — Phase II pilot-scale oxidation at midpoint conditions.
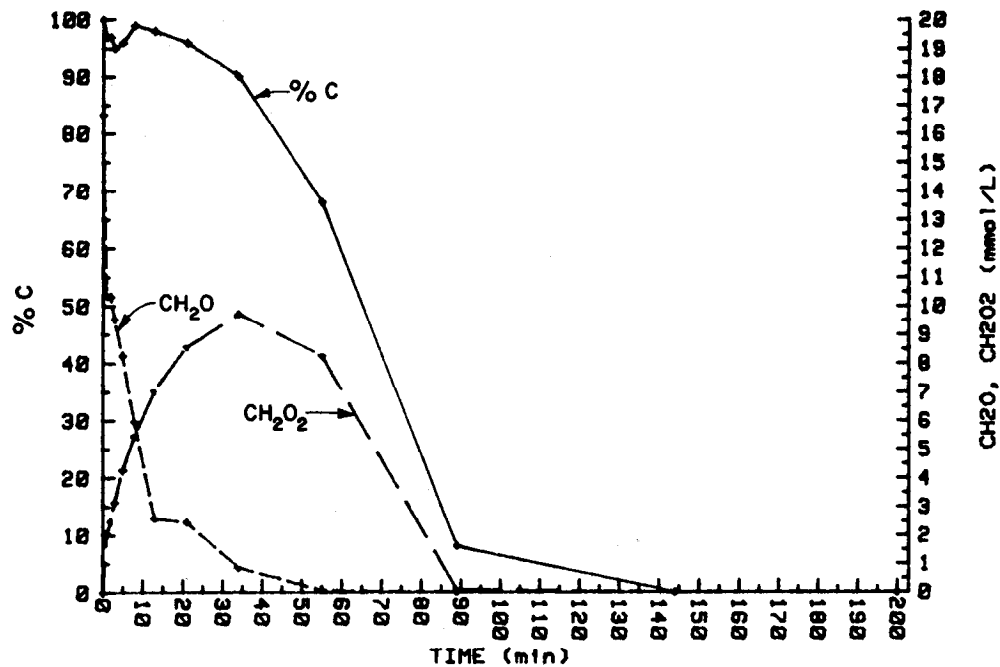
Figure 9. — Phase I bench-scale oxidation at midpoint conditions.

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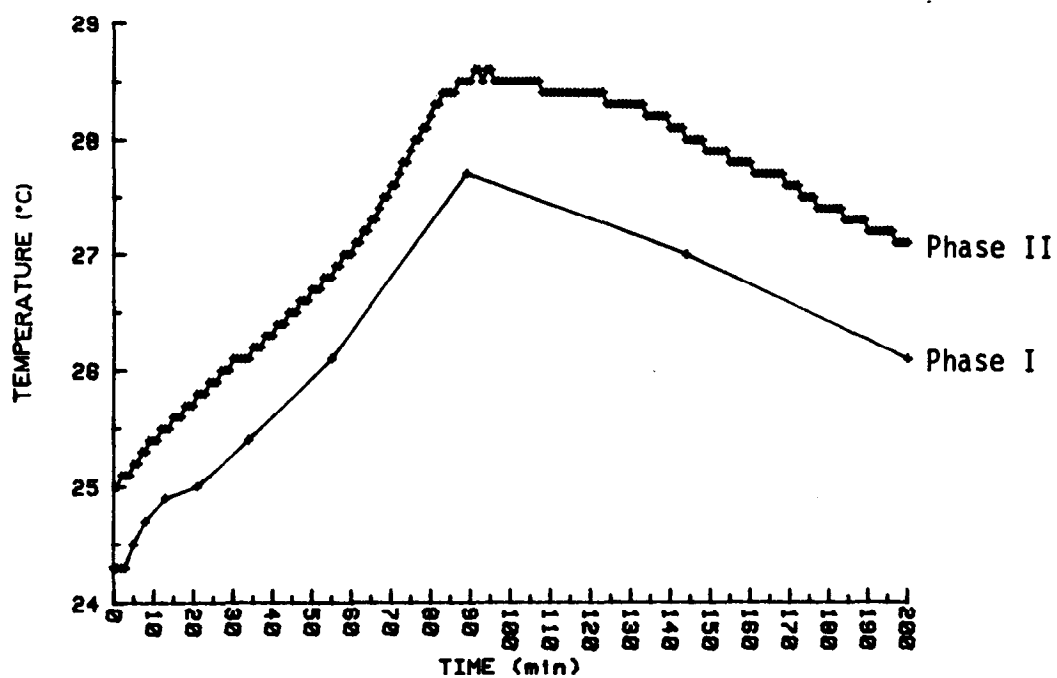
Figure 10. – Temperature variation at midpoint conditions.
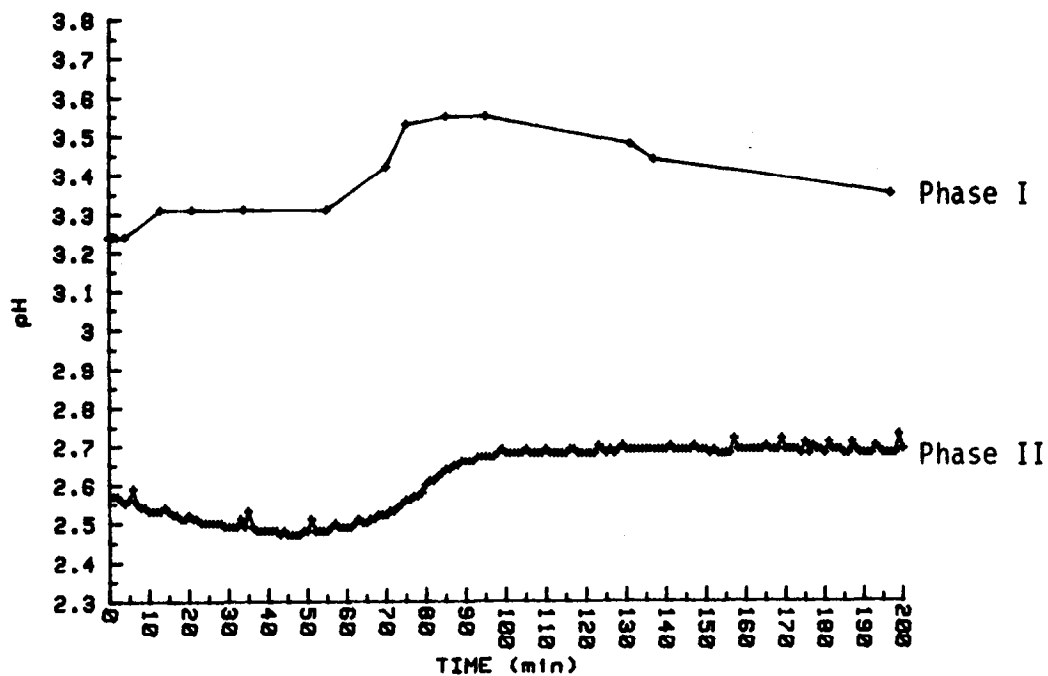
Figure 11. – Variation in pH at midpoint conditions.

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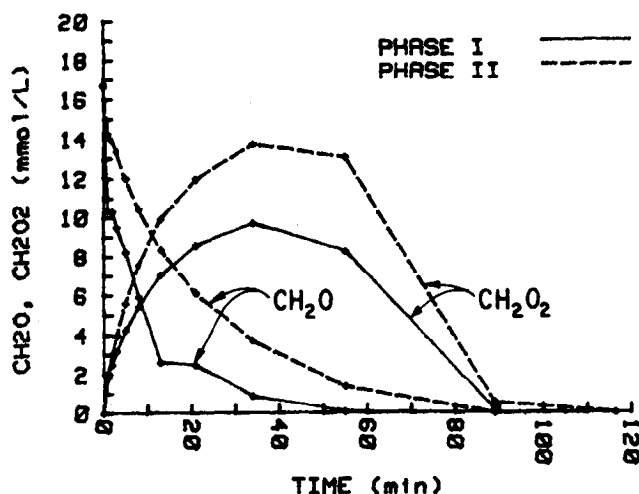
(a) Phase I test 10; phase II test 1-8 (midpoint) 16.65 mmol/L CH_2O, 99.90 mmol/L H_2O_2, 25 °C.
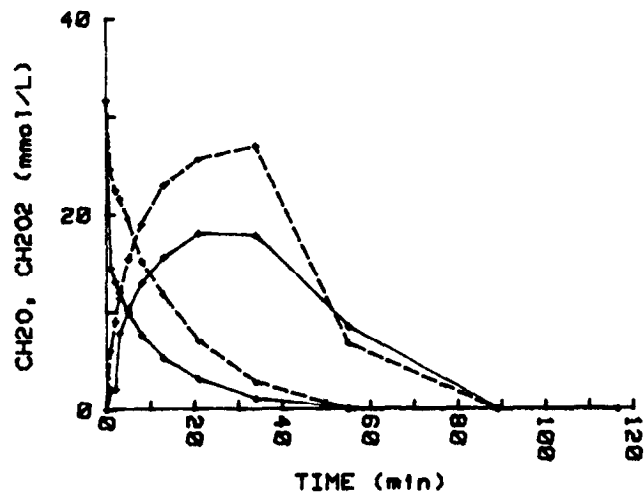
(b) Phase I test 19; phase II test 1-3 (high formaldehyde) 31.64 mmol/L CH_2O, 189.8 mmol/L H_2O_2, 25 °C.
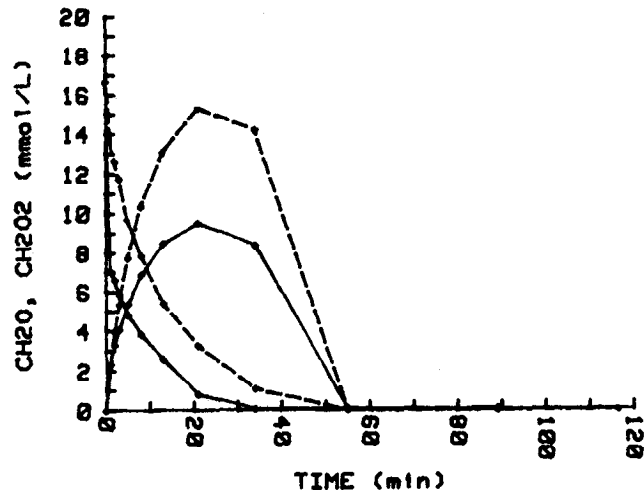
(c) Phase I test 14; phase II test 1-7 (high peroxide) 16.65 mmol/L CH_2O, 166.5 mmol/L H_2O_2, 25 °C.
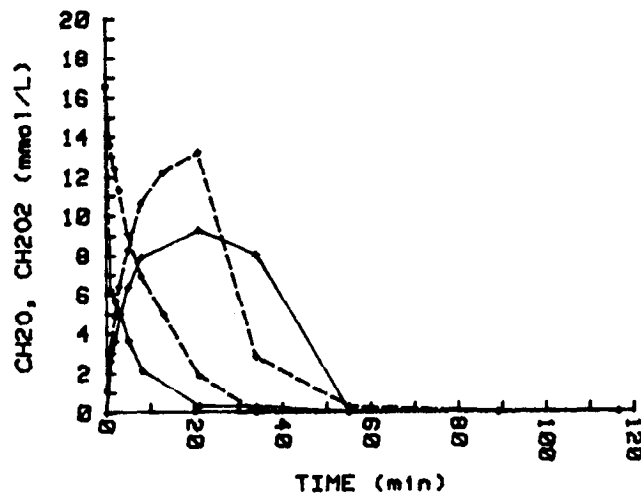
(d) Phase I test 16; phase II test 1-10 (high temperature) 16.65 mmol/L CH_2O, 99.90 mmol/L H_2O_2, 31.0 °C.

Figure 12. — Comparison of phase I bench-scale and phase II pilot-scale oxidation results at selected test conditions.

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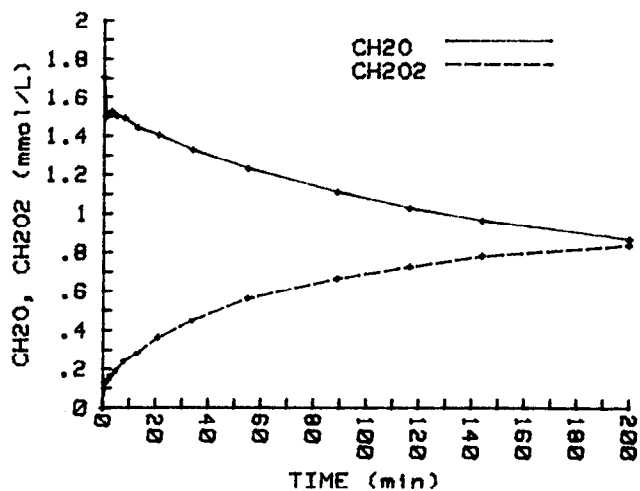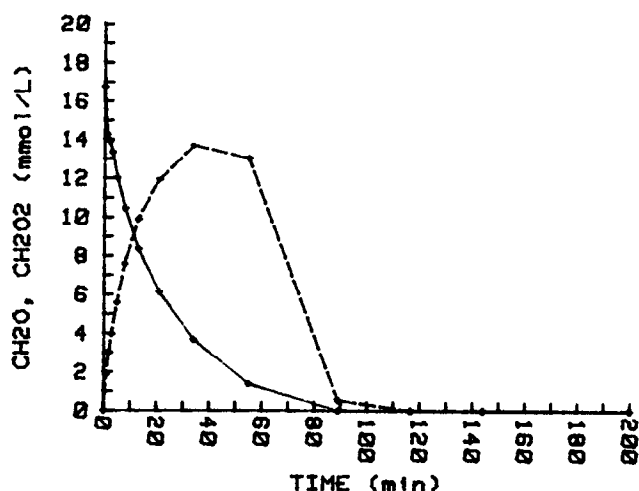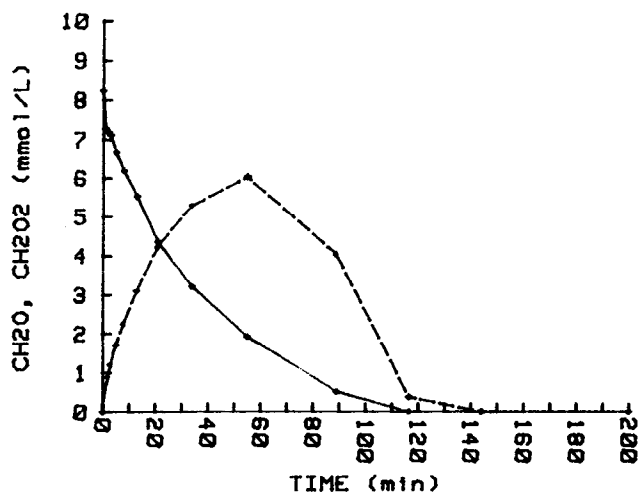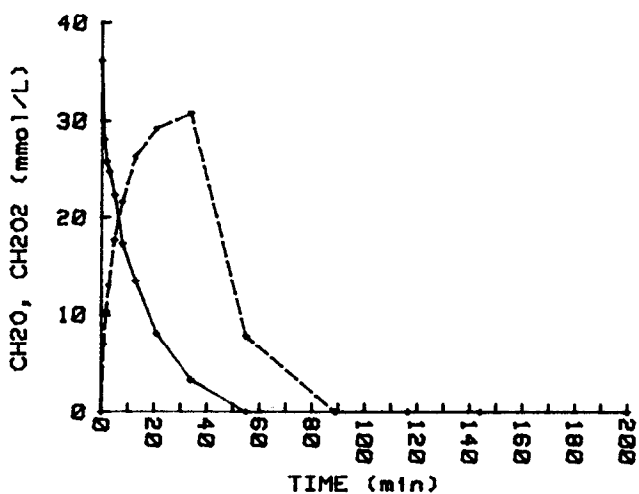
Figure 13. — Oxidation with varying CH₂O concentration at 3-times stoichiometric H_2O_2 (Fe/CH₂O = 0.2).
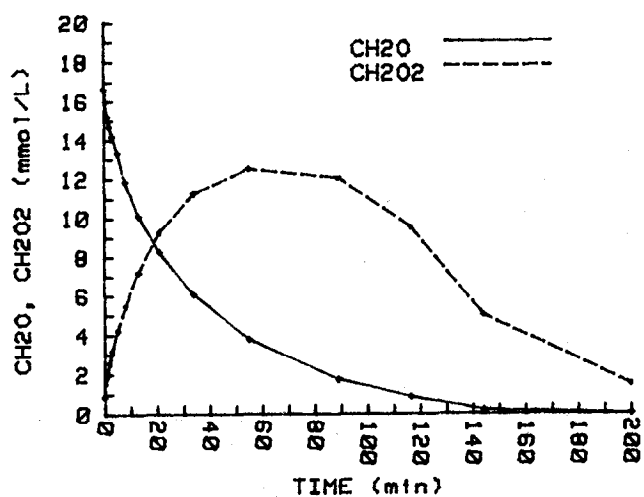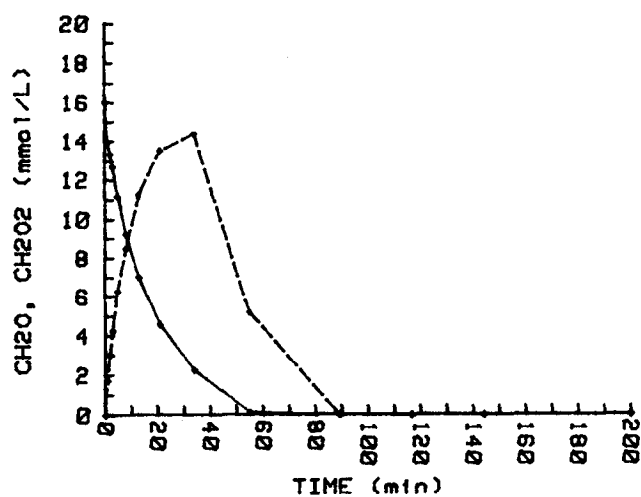
(a) 2-times stoichiometric H_2O_2.

(b) 3-times stoichiometric H_2O_2.

(c) 4-times stoichiometric H_2O_2.
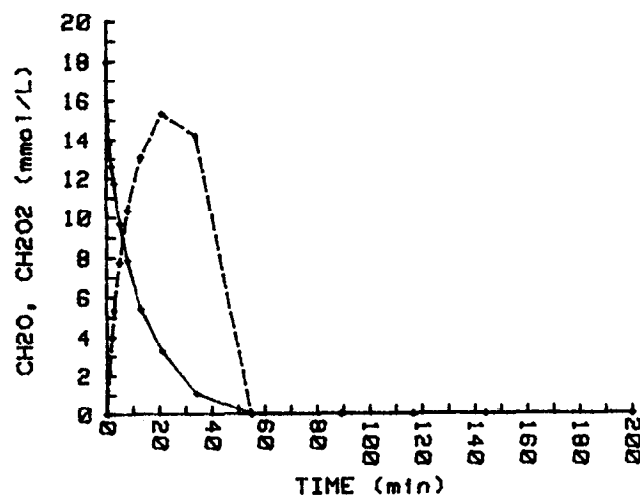
(d) 5-times stoichiometric H_2O_2.

Figure 14. — Oxidation with varying H_2O_2 concentration at 16.65 mmol/L CH_2O (Fe/CH_2O = 0.2).
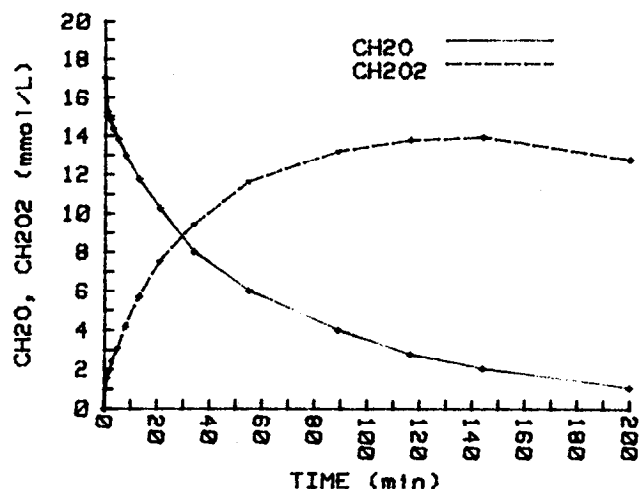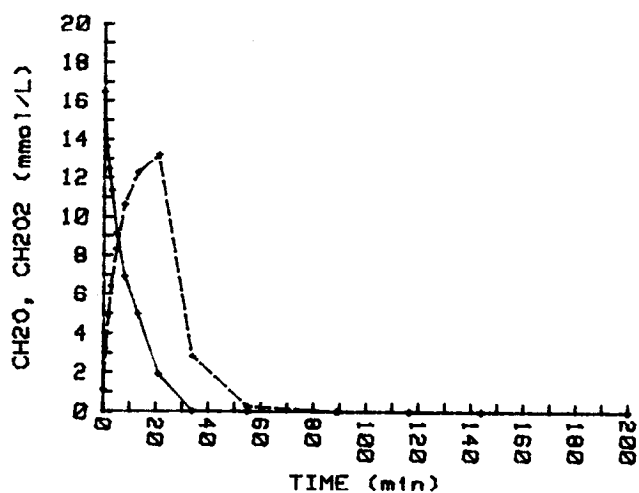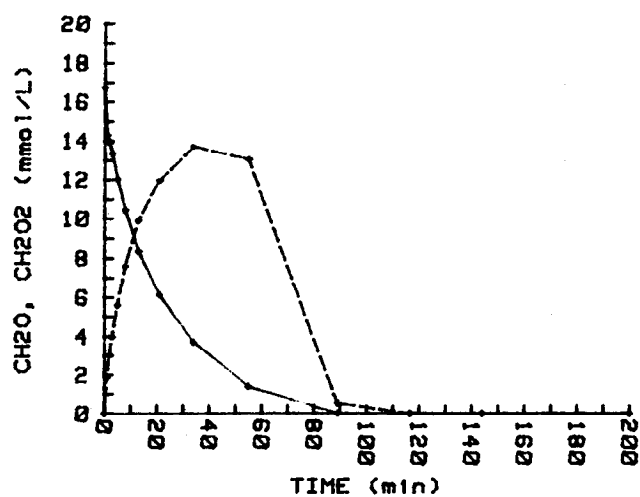
Figure 15. – Effects of initial temperature on oxidation at midpoint conditions.
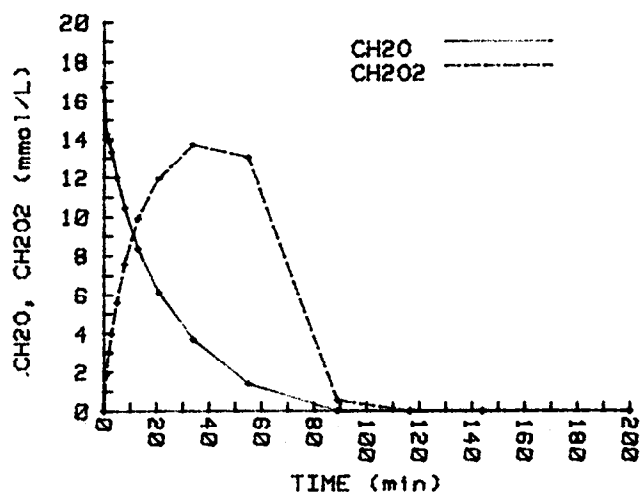
(a) Deionized water; no pH adjustment; pH before/after catalyst addition: 4.63/2.56.

(b) TDS = 300 mg/L; no pH adjustment; pH before/after catalyst addition: 6.86/2.60.
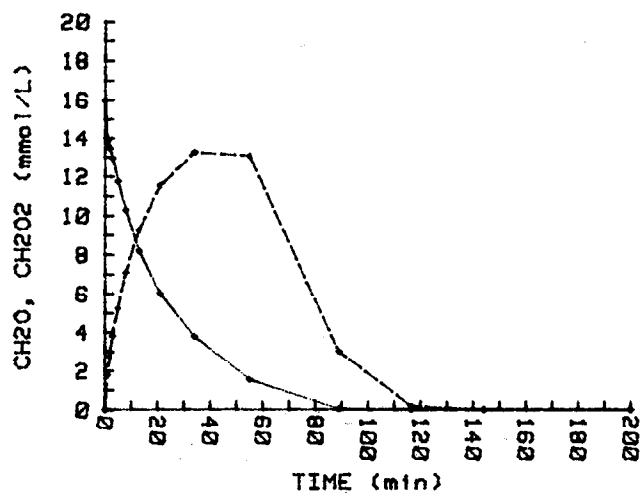
(c) TDS = 300 mg/L; pH adjusted before catalyst addition; pH before/after catalyst addition: 4.44/2.62.
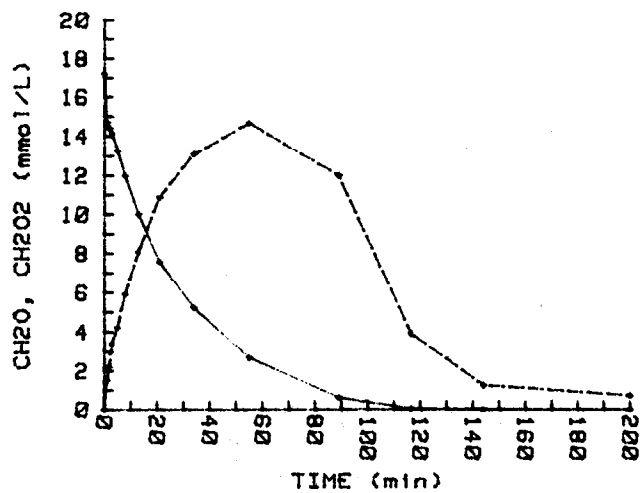
(d) TDS = 300 mg/L; pH adjusted before catalyst addition; pH before/after catalyst addition: 2.71/2.43.

Figure 16. – Effects of background TDS equivalent to Yuma service water compared with deionized water.
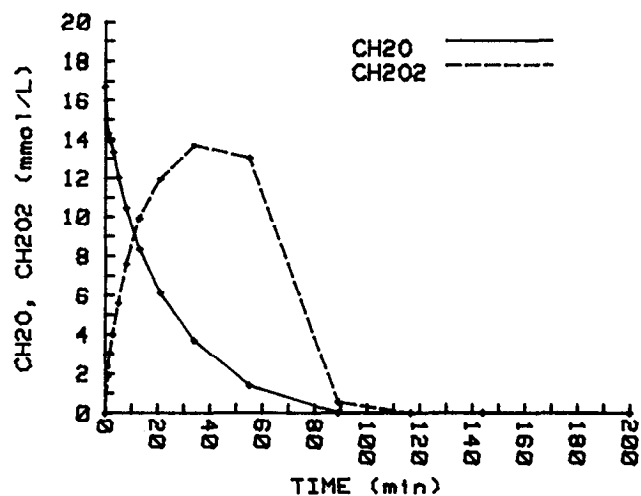
(a) Deionized water; no pH adjustment; pH before/after catalyst addition: 4.63/2.56.

(b) TDS = 3000 mg/L; no pH adjustment; pH before/after catalyst addition: 9.11/2.62.
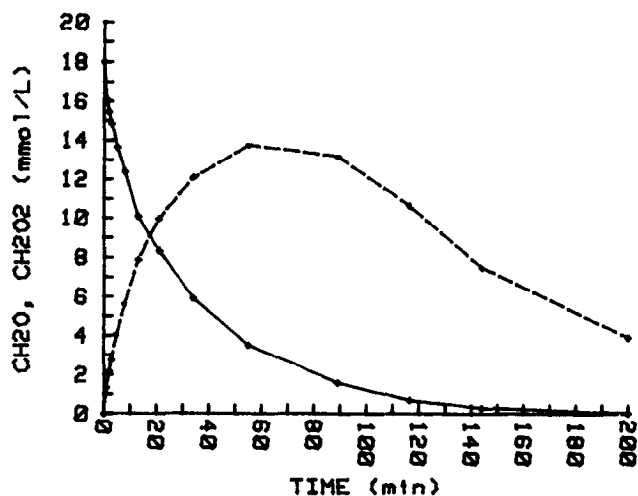
(c) TDS = 3000 mg/L; pH adjusted prior to catalyst addition; pH before/after catalyst addition: 4.61/2.73.
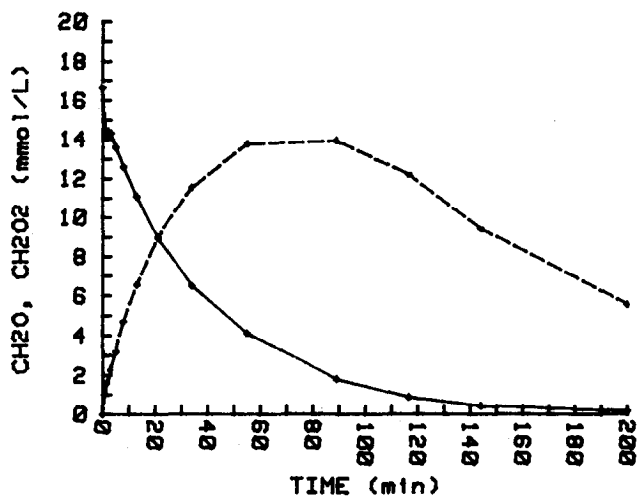
(d) TDS = 3000 mg/L; pH adjusted before catalyst addition; pH before/after catalyst addition: 2.63/2.42.

Figure 17. — Effects of background TDS equivalent to 10 times the concentration of Yuma service water compared with deionized water.

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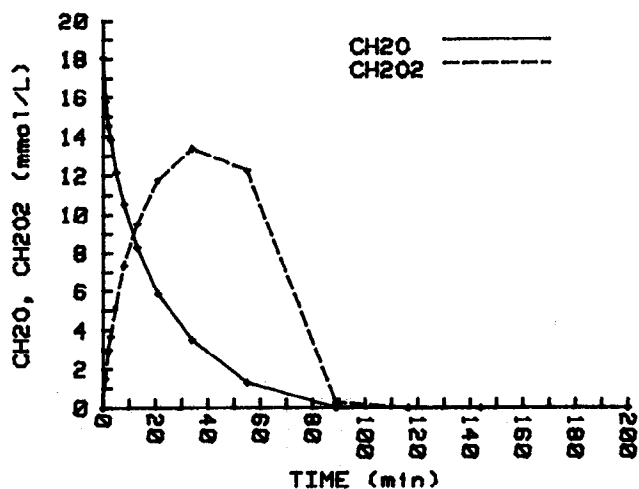
(a) Stirring power input of 0.0005 W/L.
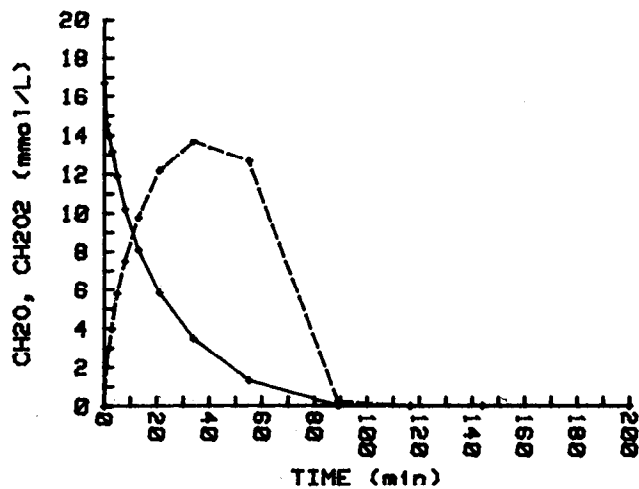
(c) Stirring power input of 0.05 W/L.
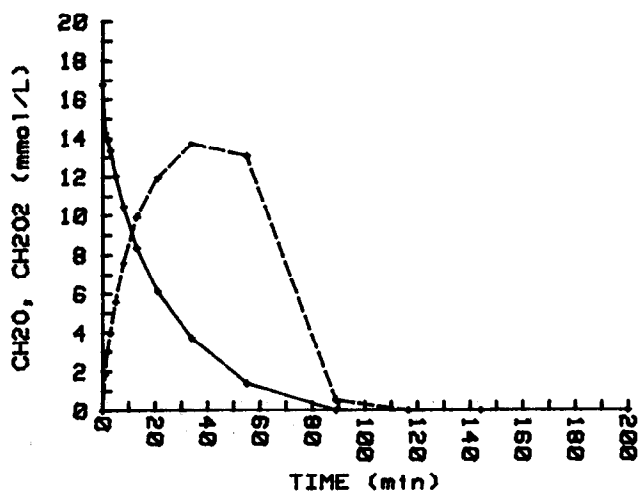
(b) Stirring power input of 0.005 W/L.

Figure 18. – Effects of stirring power input on oxidation at midpoint conditions.
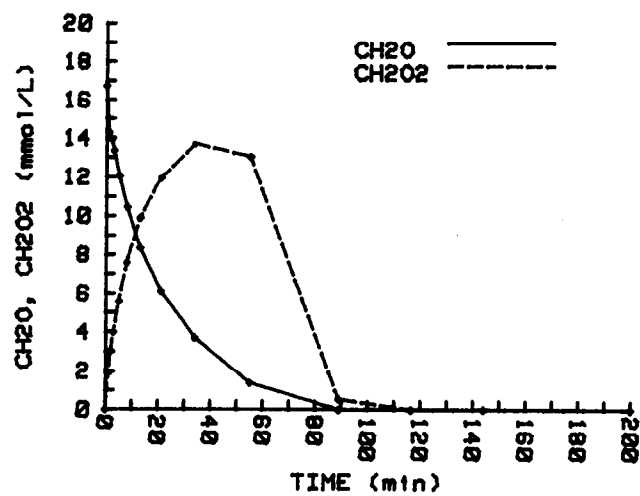
(a) Batch H₂O₂ addition.
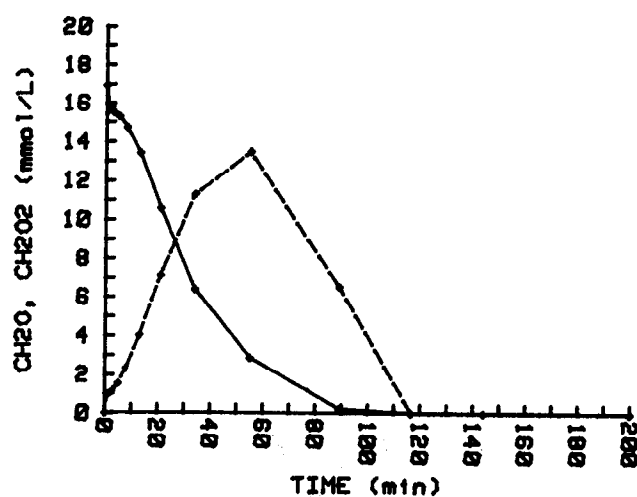
(b) 15-minute H₂O₂ metering.
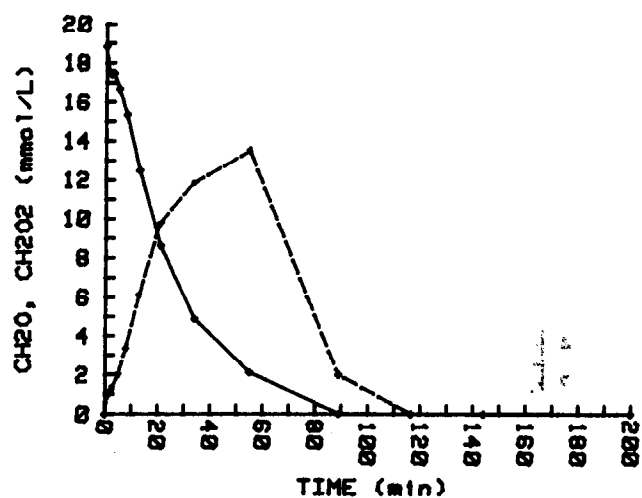
(c) 30-minute H₂O₂ metering.
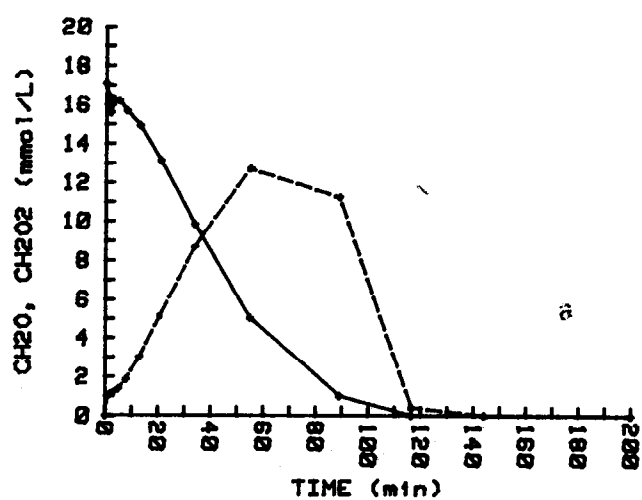
(d) 60-minute H₂O₂ metering.

Figure 19. – Effects of metering 3-times stoichiometric H₂O₂ compared with batch addition.
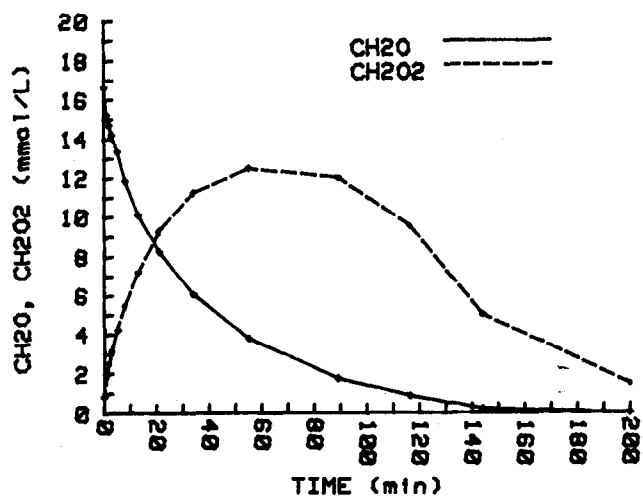
(a) Batch H_2O_2 addition.
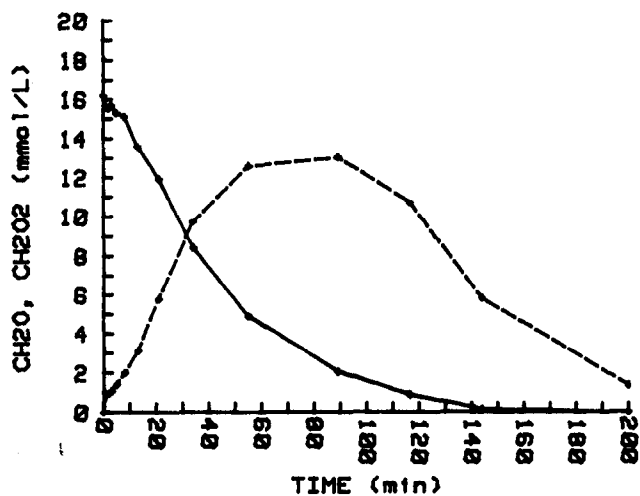
(b) 15-minute H_2O_2 metering.
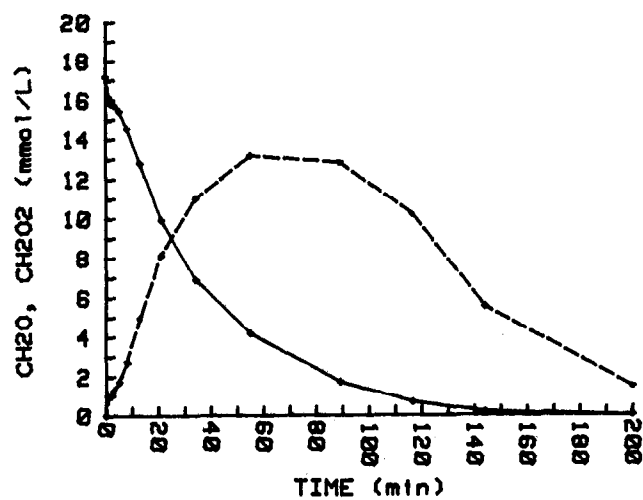
(c) 30-minute H_2O_2 metering.
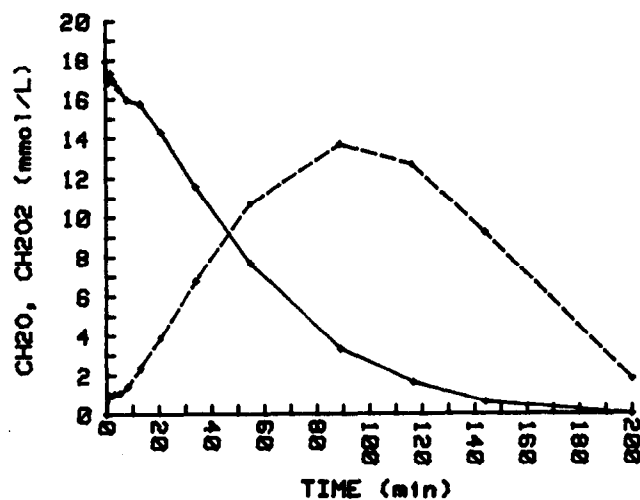
(d) 60-minute H_2O_2 metering.

Figure 20. – Effects of metering 2-times stoichiometric H_2O_2 compared with batch addition.

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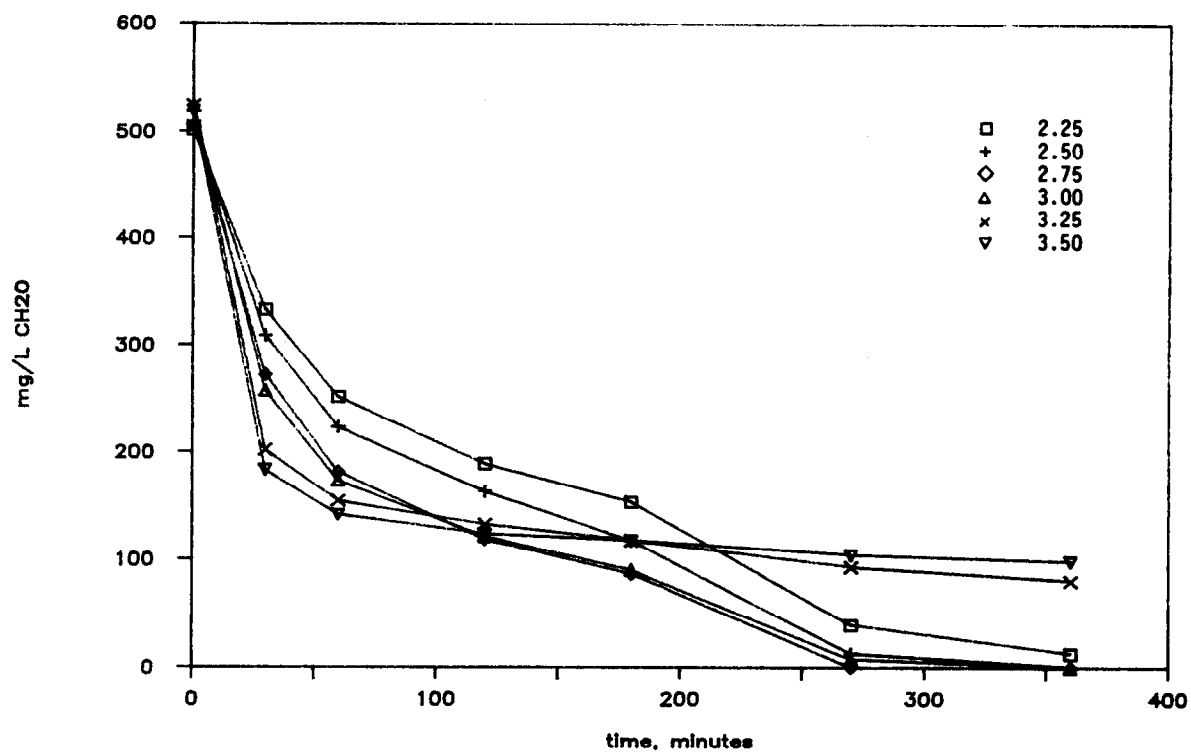
(a) Formaldehyde concentration versus initial pH.
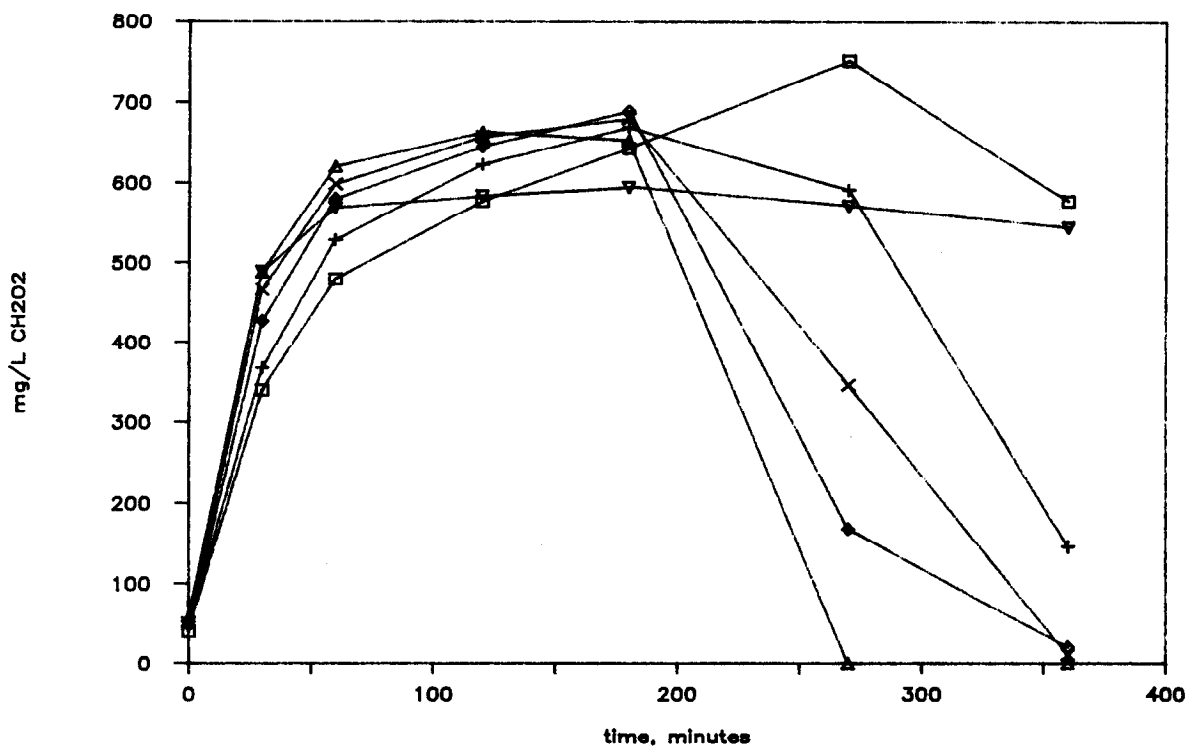
(b) Formate concentration versus initial pH.

Figure 21. — Effect of starting pH on the reaction.

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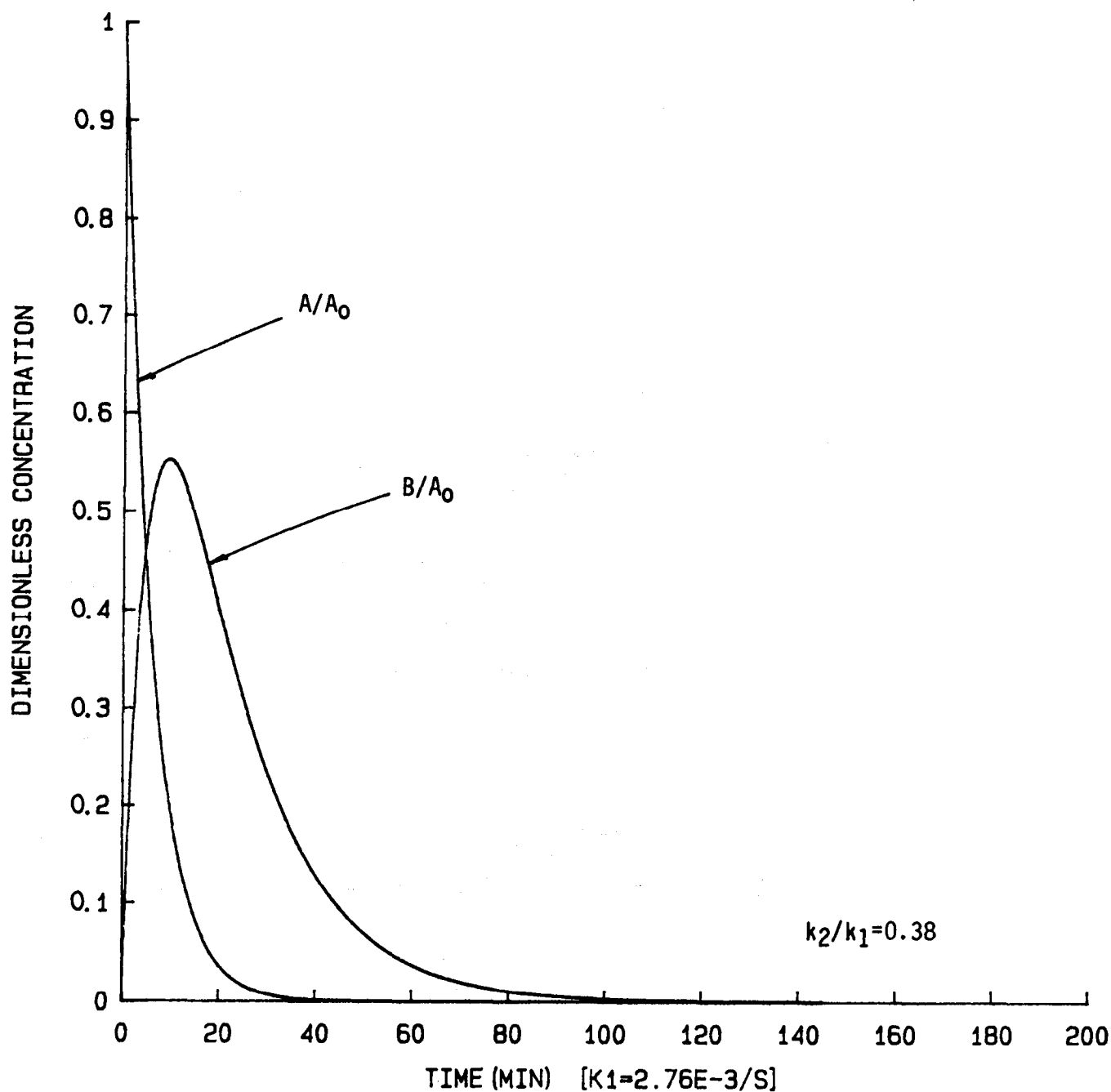
Figure 22. — Series first-order reaction representing the oxidation of formaldehyde (A) to formic acid (B). At constant temperature (25 °C), pH (approx. 3.3), ferric chloride concentration (3.33 mmol/L), and hydrogen peroxide concentration (99.90 mmol/L) with rate coefficients estimated from phase I tests.

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(a) Isothermal test 46 (midpoint).

CONCENTRATION (mmol/L)

TIME (min)

(b) Isothermal test 46 (midpoint).

H2O2 EFFICIENCY

TIME (min)
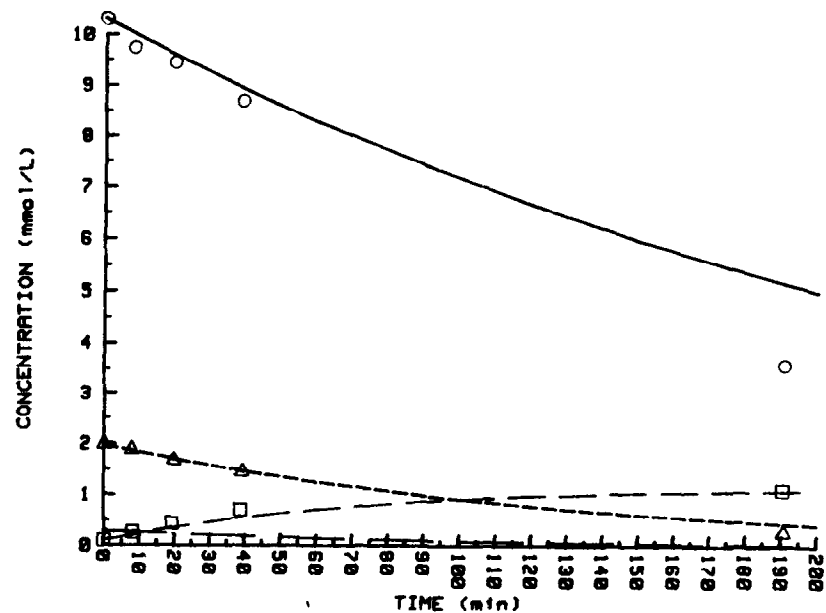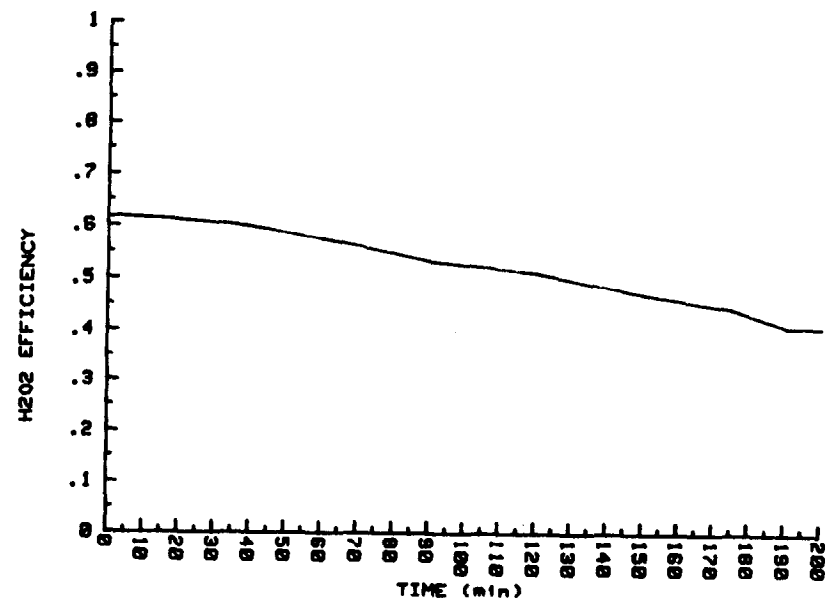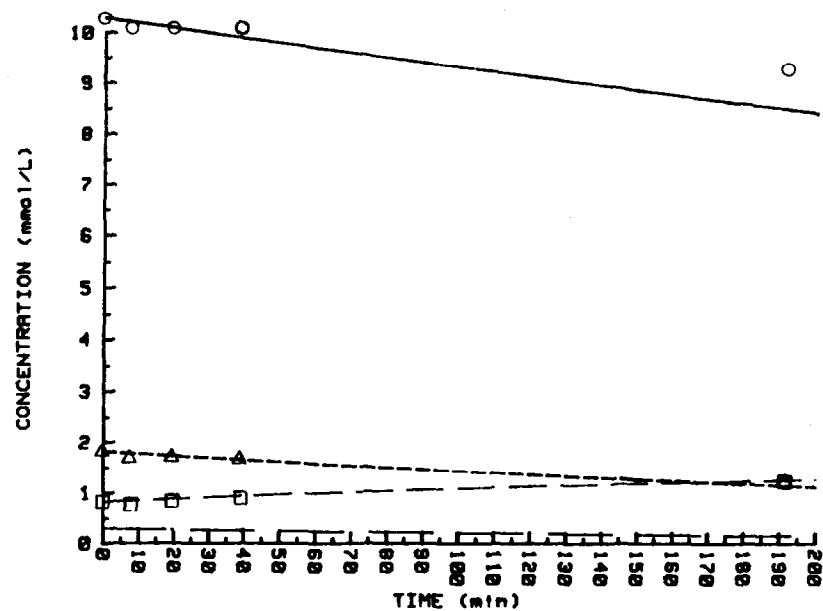
(c) Isothermal test 51 (high Na_2SO_4).

CONCENTRATION (mmol/L)

TIME (min)
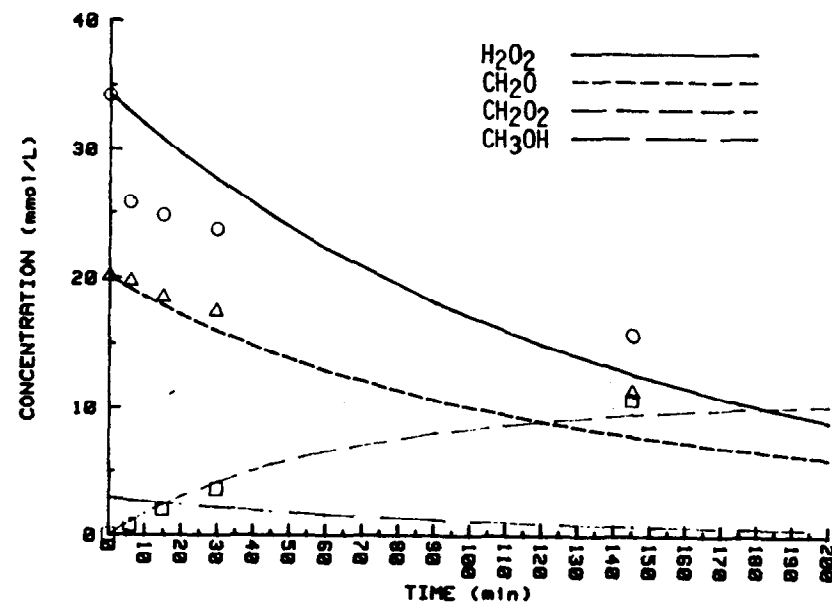
(d) Isothermal test 17 (high H_2O_2, high CH_2O).

CONCENTRATION (mmol/L)

TIME (min)

H_2O_2
CH_2O
CH_2O_2
CH_3OH

Figure 23. – Sixteen-parameter model predictions compared with test data for selected isothermal test conditions.
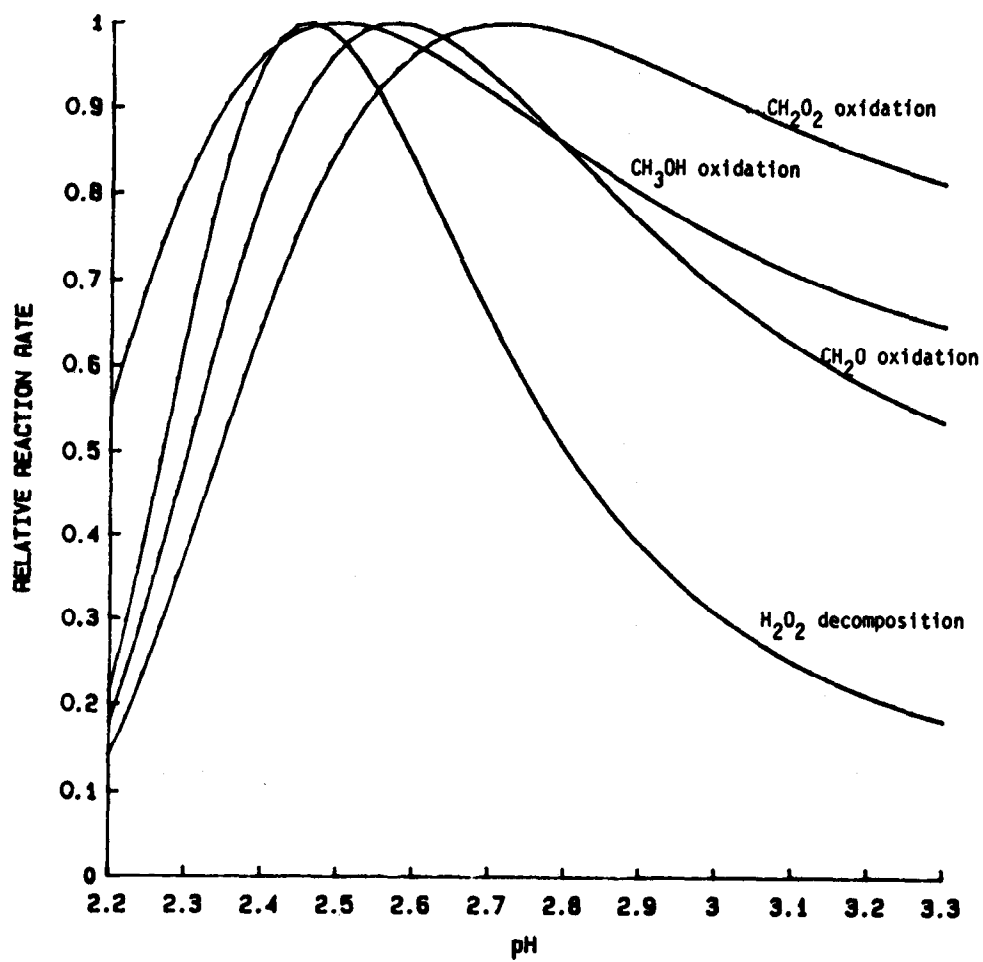
Figure 24. – Dependence of reaction rate on pH as estimated by the 36-parameter model.
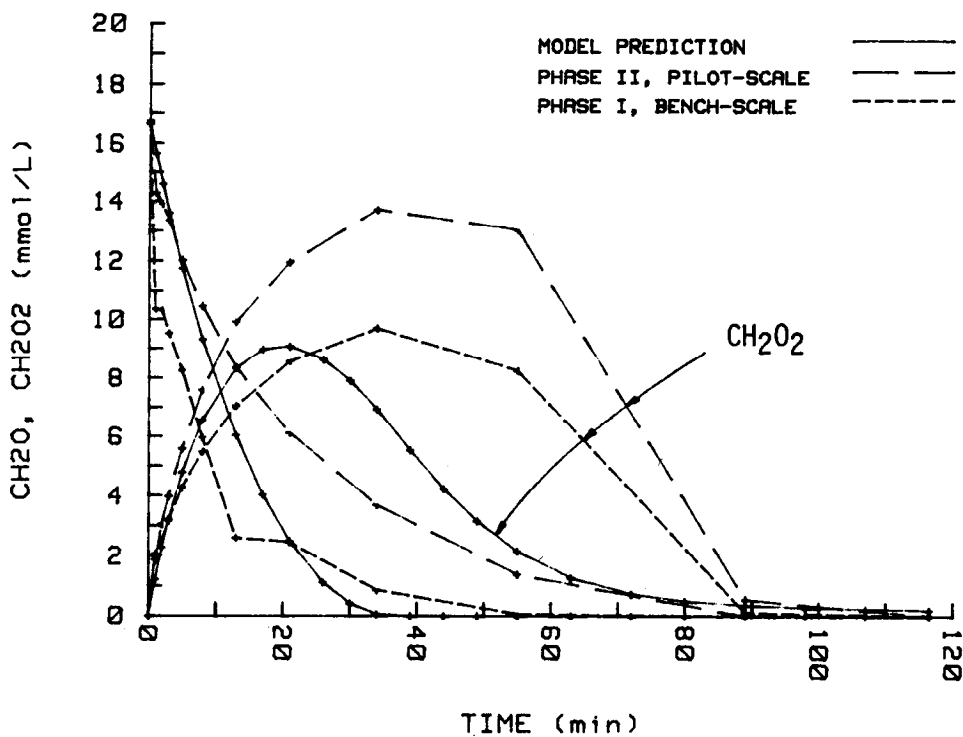
(a) Formaldehyde and formate.
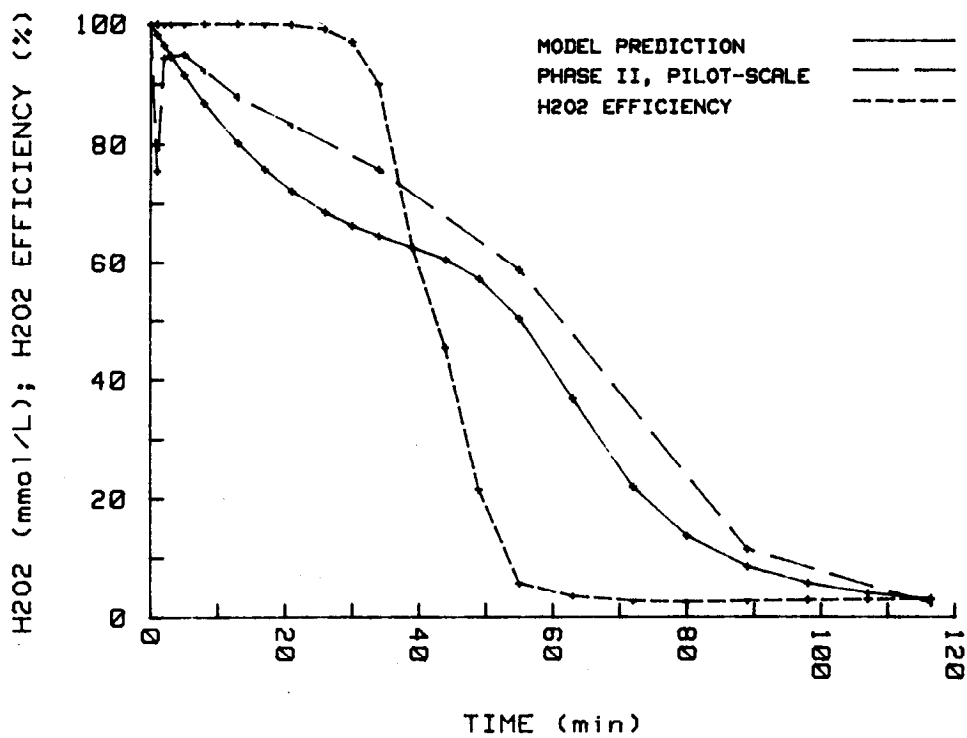
(b) Hydrogen peroxide.

Figure 25. — Sixteen-parameter model predictions compared with test data for the phase I bench-scale and phase II pilot-scale (adiabatic) midpoint test conditions.

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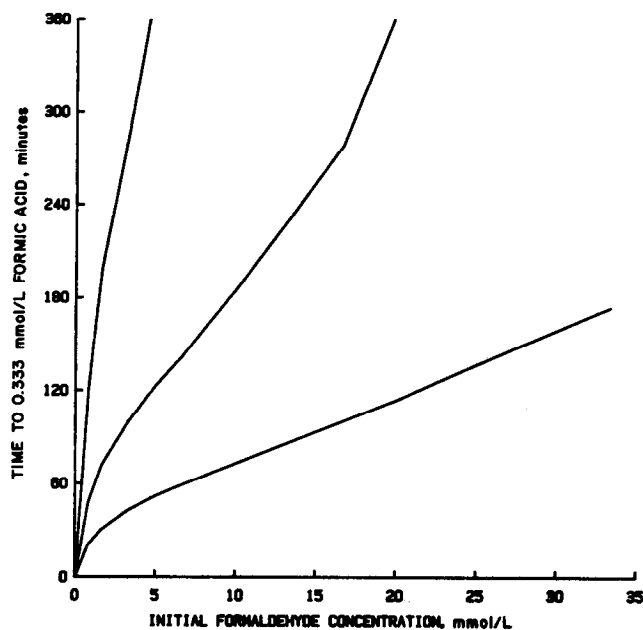
(a) To a formic acid concentration of 0.033 mmol/L; 1.00 mmol/L Fe+3.
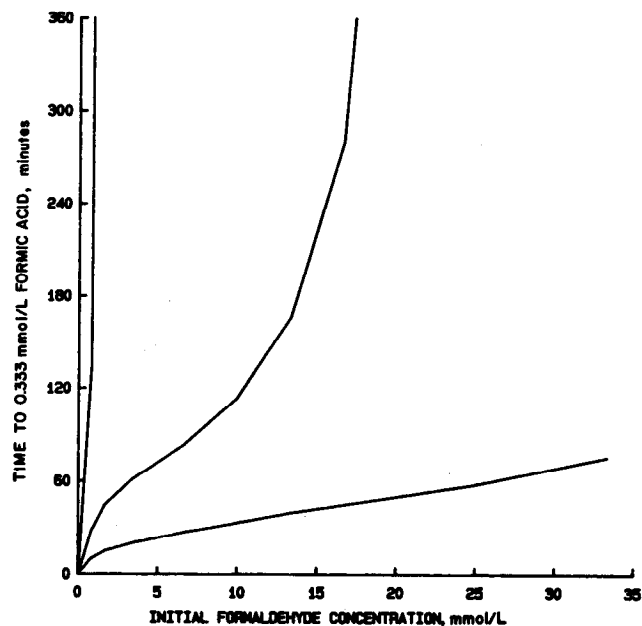
(b) To a formic acid concentration of 0.033 mmol/L; 3.33 mmol/L Fe+3.
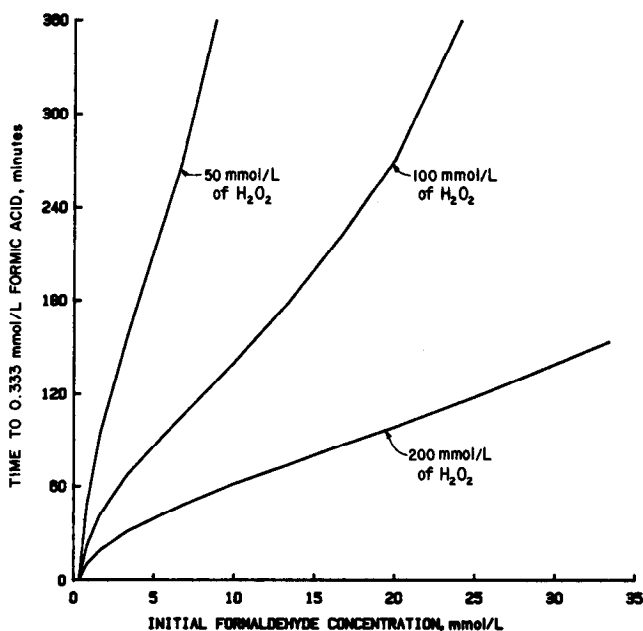
(c) To a formic acid concentration of 0.333 mmol/L; 1.00 mmol/L Fe+3.
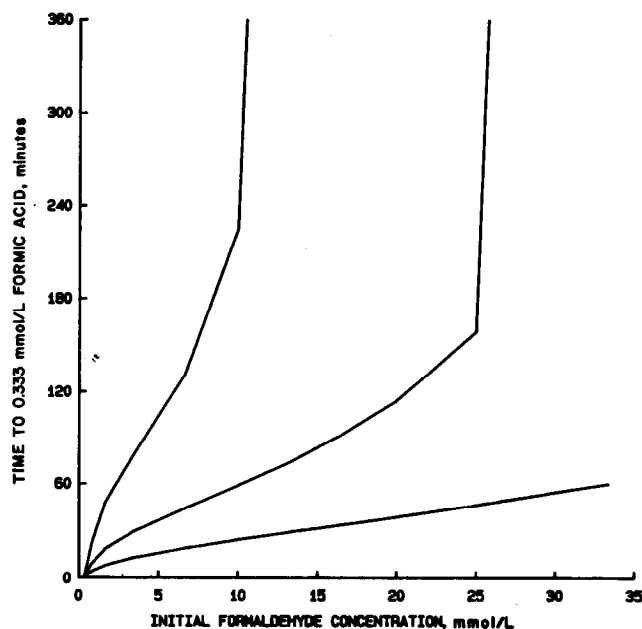
(d) To a formic acid concentration of 0.333 mmol/L; 3.33 mmol/L Fe+3.

Figure 26. — Total reaction times required to oxidize formaldehyde storage solutions to a formic acid concentration of 0.033 mmol/L (1.5 mg/L) and 0.333 mmol/L (15 mg/L) as predicted by the 16-parameter model.

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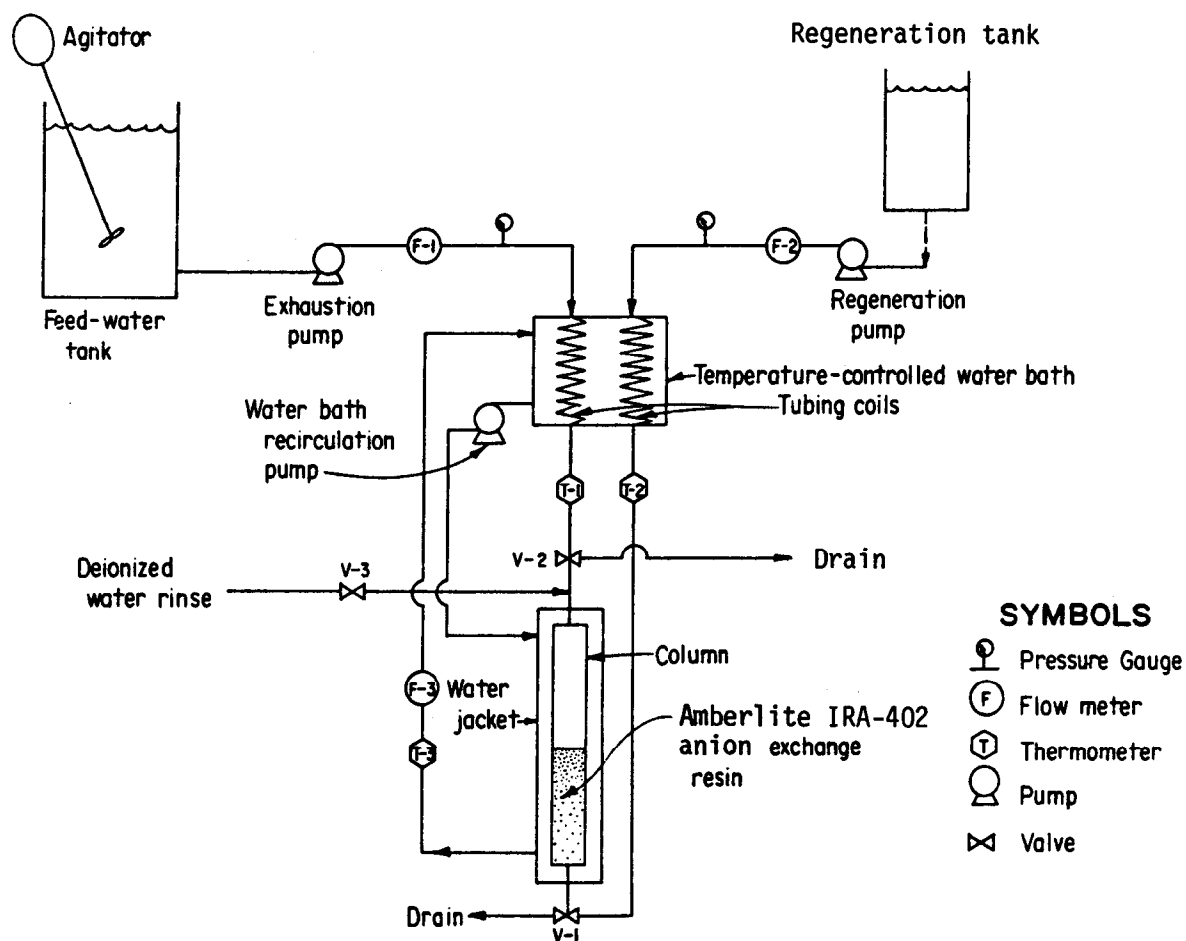
Figure 27. — Schematic of dynamic ion exchange experimental apparatus.
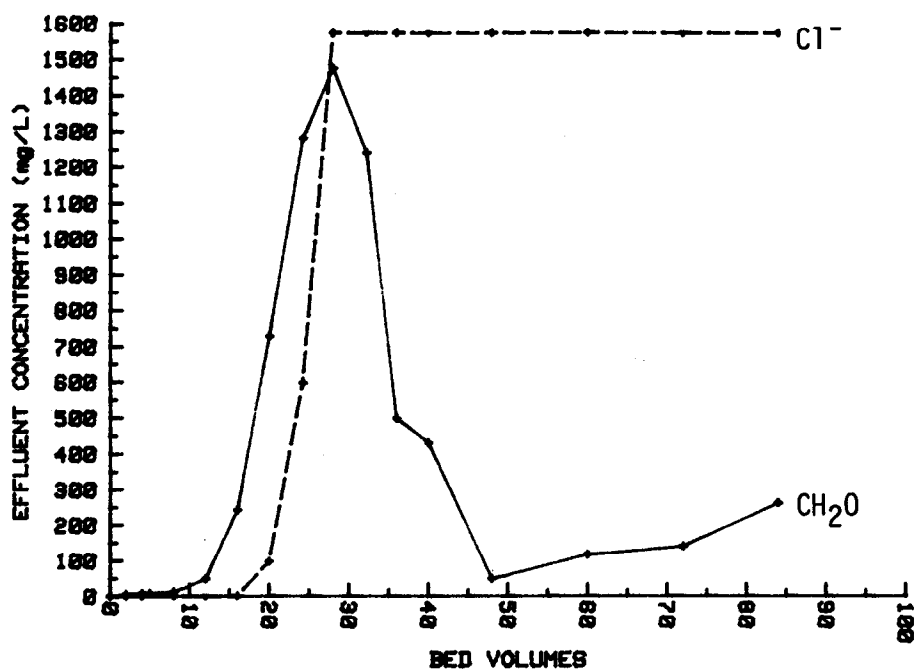
Figure 28. — Concentration profile for dynamic test 1.

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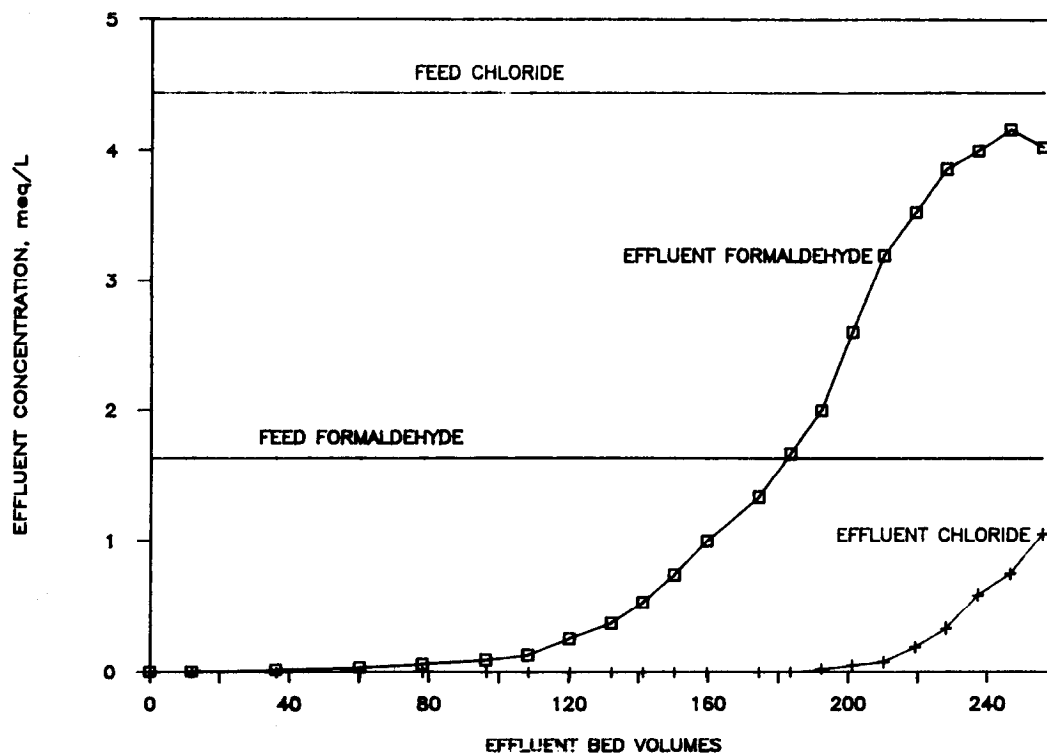
(a) Expressed in terms of meq/L.
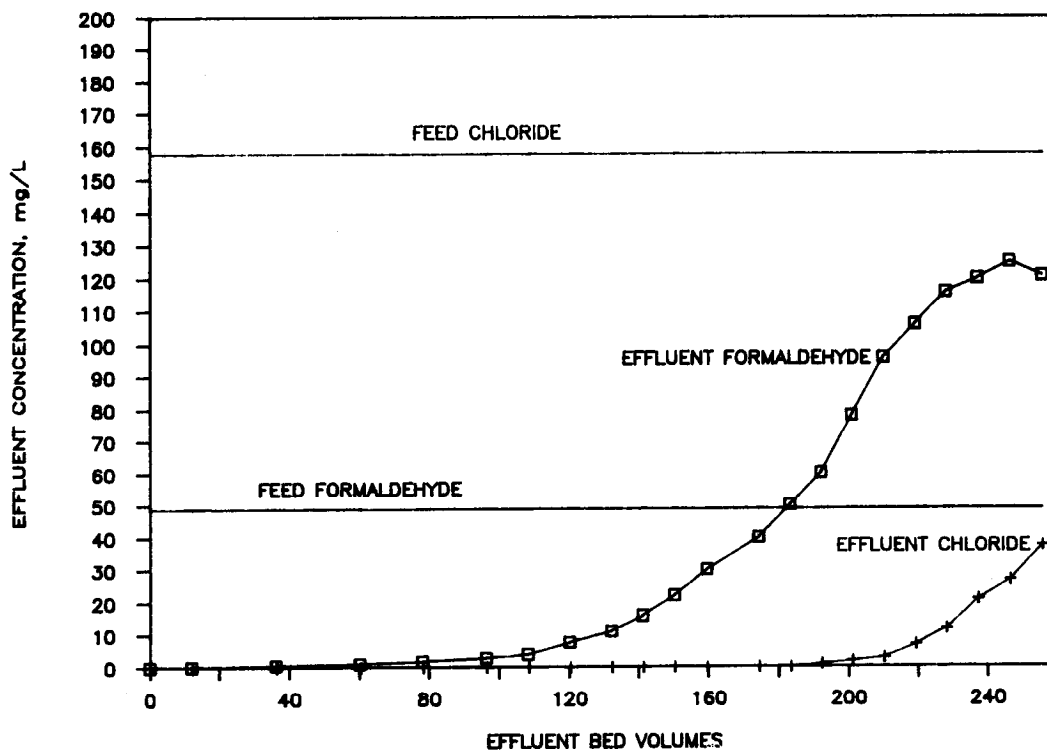
(b) Expressed in terms of mg/L.

Figure 29. – Concentration profile for dynamic test 2. Feed solution: 48.9 mg/L CH_2O, 158 mg/L Cl, and 10 mg/L SO_4.

44
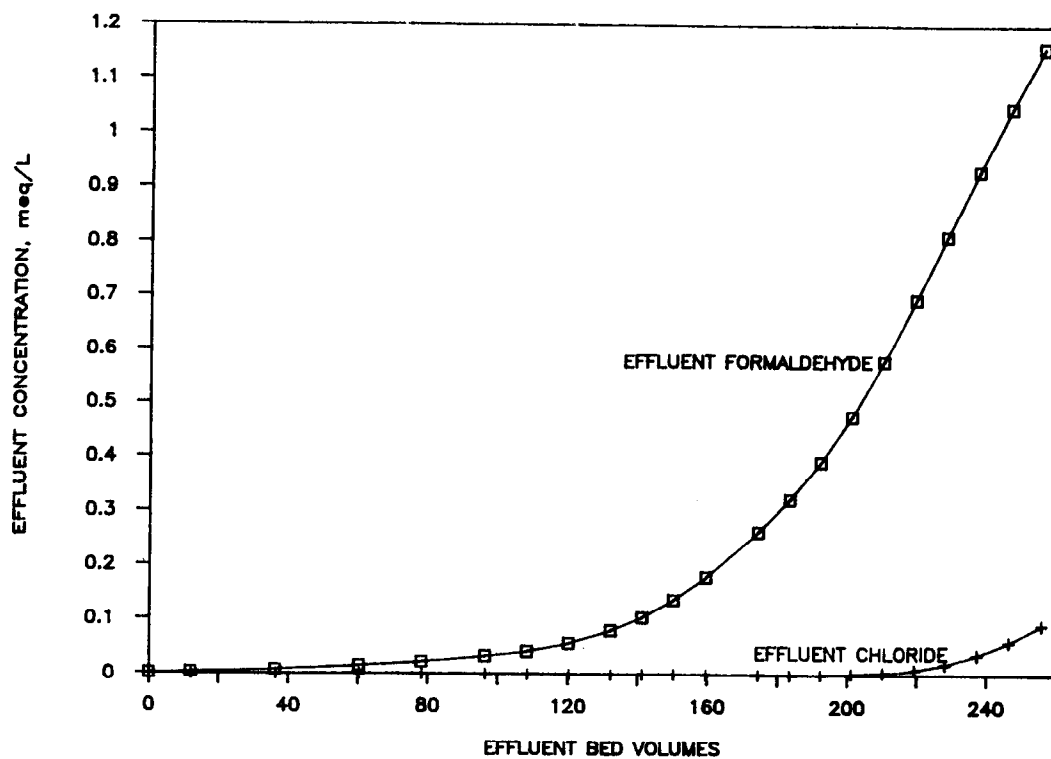
(a) Expressed in terms of meq/L.
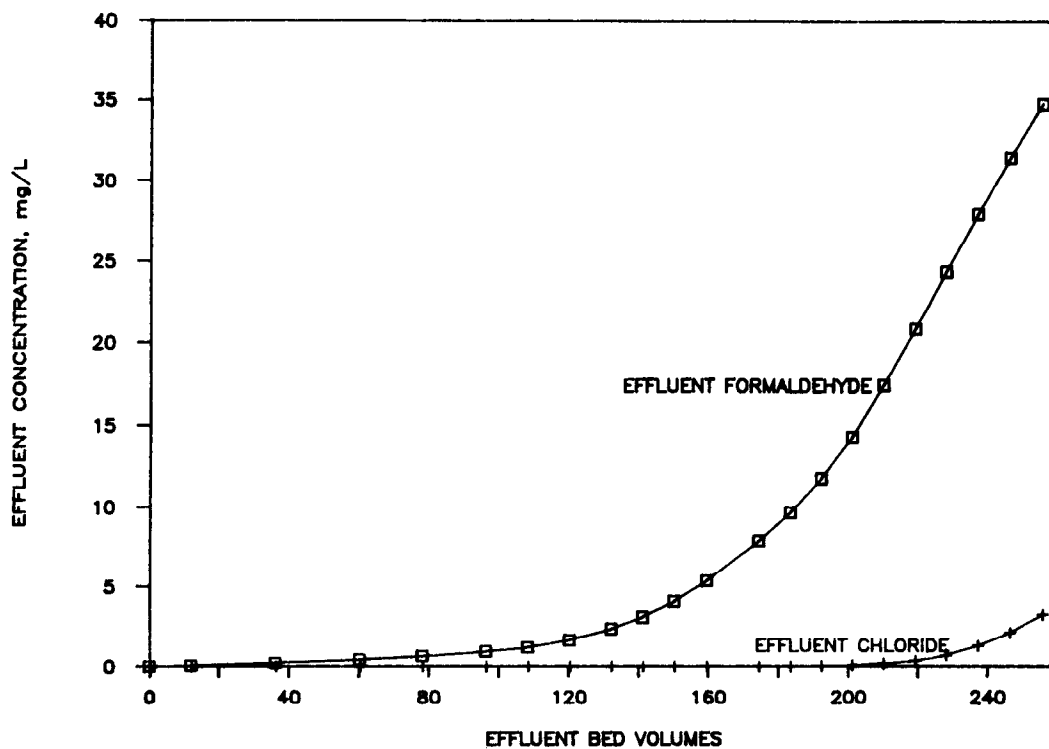
(b) Expressed in terms of mg/L.

Figure 30. – Accumulated average formaldehyde and chloride ion leakage for dynamic test 2.
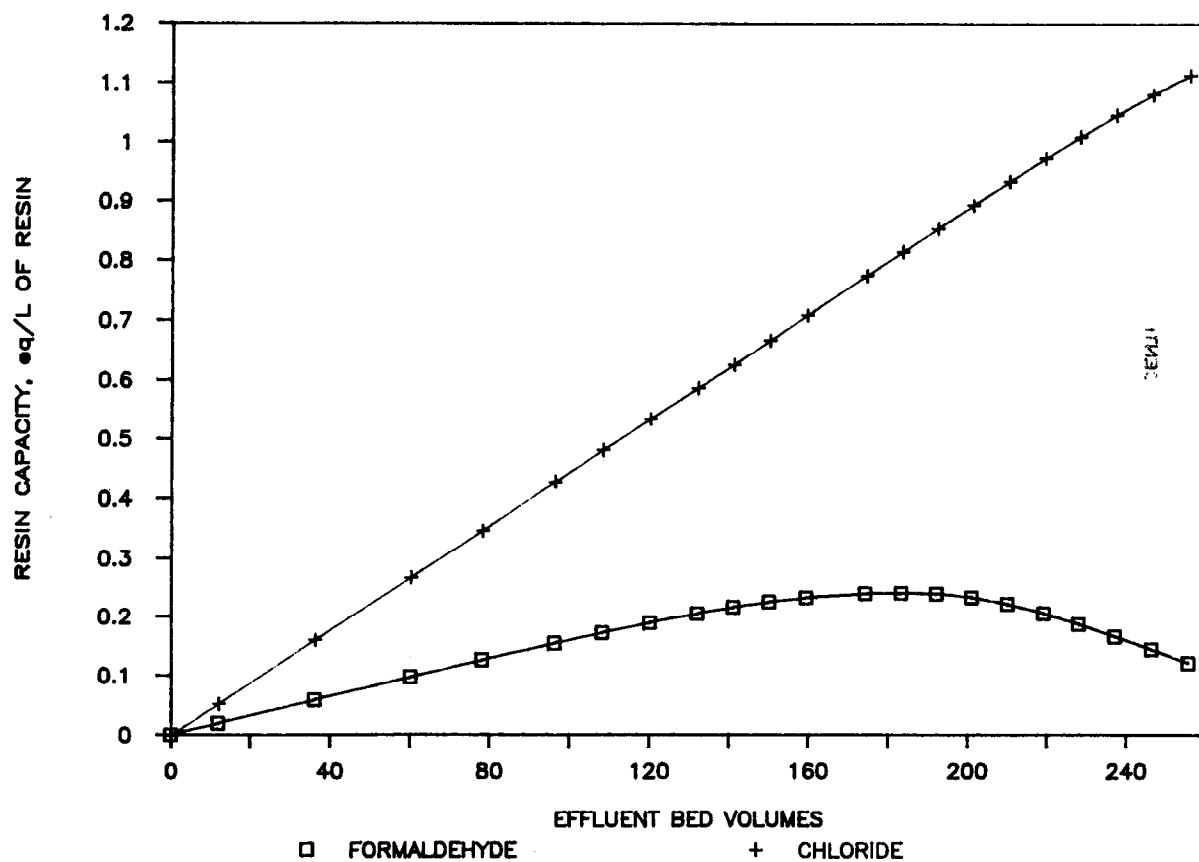
Figure 31. – Formaldehyde and chloride resin capacity for dynamic test 2.

APPENDIX A

EXPERIMENTS TO VERIFY REACTION STOICHIOMETRY

Background

Previous work documented in Bureau publication REC-ERC-84-8 [1] supports the fact that formaldehyde oxidizes to formic acid and then to carbon dioxide gas in the ferric chloride/hydrogen peroxide system. Recent results show that methanol oxidizes to formaldehyde. Therefore, oxidation of formaldehyde solutions that contain methanol as a stabilizer must have all three organic reactions occurring together.

Although much effort has been spent on the empirical aspects of the reaction, the basic questions regarding what is the correct stoichiometry has remained unanswered. In the past, the chemical equations assumed to have described the process were as follows:

$$CH_3OH + 3H_2O_2 \longrightarrow CO_2 + 5H_2O \quad \text{(A1)}$$
$$CH_2O + 2H_2O_2 \longrightarrow CO_2 + 3H_2O \quad \text{(A2)}$$
$$CH_2O_2 + H_2O_2 \longrightarrow CO_2 + 2H_2O \quad \text{(A3)}$$
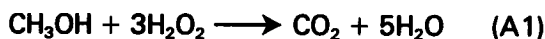
These reactions were derived assuming that minimum hydrogen peroxide is needed to achieve the oxidation. However, there exists an infinite number of balanced reactions that could be written as follows:

$$CH_3OH + xH_2O_2 \longrightarrow CO_2$$
$$+ [(x-3)/2]O_2 + (x+2)H_2O \quad \text{(A4)}$$

$$CH_2O + yH_2O_2 \longrightarrow CO_2$$
$$+ [(y-2)/2]O_2 + (y+1)H_2O \quad \text{(A5)}$$

$$CH_2O_2 + zH_2O_2 \longrightarrow CO_2$$
$$+ [(z-1)/2]O_2 + (z+1)H_2O \quad \text{(A6)}$$
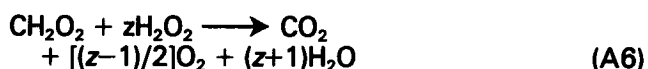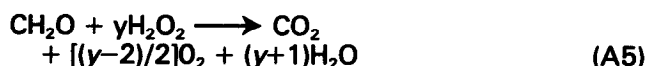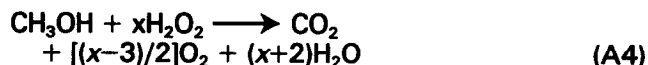
Ideally, if equations (A1), (A2), and (A3) could be shown experimentally to be correct, then any additional peroxide is wasted through decomposition to oxygen and water. If more peroxide than the minimum is needed, then either additional peroxide is required as part of the reaction mechanism or conditions of the experiment were such that excess peroxide was consumed by decomposition.

Experimental Procedures

Methanol. — The experimental work to validate equation (A1) began with twelve 1-liter containers each filled with a liter of deionized water, followed by the addition of 0.81 grams of $FeCl_3 \cdot 6H_2O$ and 593 microliters of methanol. This resulted in a solution consisting of 0.0030M $FeCl_3 \cdot 6H_2O$ and 0.015M methanol, which yielded a Fe/CH_3OH molar ratio of 0.2. According to our previous work, this molar ratio was found to minimize peroxide loss caused by decomposition with formaldehyde, and is assumed to be the preferred ratio with methanol. The solution used was tagged with ^{14}C methanol. Increasing ratios of peroxide to methanol were added to each bottle. The samples were kept loosely capped in a hood for 48 hours at a total temperature variation of approximately 20 to 25 °C. Scintillation counts were then determined for each of the samples as shown in table A-1 (a.1) and on figure A-1. These data show that quantitative oxidation occurs at a $[H_2O_2/CH_3OH]$ ratio of 4, instead of the expected ratio of 3.

Oxygen gas collected from the reaction accounted for the additional peroxide used. However, it is unknown whether the oxygen was liberated as a result of the oxidation of the organic species present or from the decomposition of peroxide, independent of the organic species.

Another experiment was conducted in which formate, the known oxidation product before carbon dioxide production, was measured. Eight bottles were filled with 1 liter of deionized water, followed by the addition of 593 microliters of methanol and 0.20 grams of $FeCl_3 \cdot 6H_2O$. All other conditions were the same as in the previous test. The results of this experiment, shown in table A-1(a.2), again show a molar ratio of 4.

Formaldehyde. — Bottles with a capacity of approximately 200 mL were filled with 100 mL of 0.015M formaldehyde solution, followed by the addition of 1 mL of 8.1-percent $FeCl_3 \cdot 6H_2O$. Increasing ratios of peroxide to formaldehyde were then added to each bottle from a 30-percent stock solution. The samples were kept loosely capped in a hood for 48 hours at a total temperature variation of approximately 20 to 25 °C. Table A-1(b.1) shows the resulting measurements of formaldehyde and formate.

Based on the assay of the stock formaldehyde, the solution used to generate table A-1(b.1) had 0.567 moles of methanol. This led to the results shown in

Table A-1. — Results of experiments to determine reaction stoichiometry.

$\dfrac{[H_2O_2]}{[CH_3OH]}$	$\dfrac{[H_2O_2]}{[CH_2O]}$	$\dfrac{[H_2O_2]}{[CH_2O_2]}$	CH_2O, mmol	CH_2O_2, mmol	Percent ^{14}C remaining	Percent CH_2O_2 remaining	Residual H_2O_2	pH
(a.1) Methanol:								
1.0					74.0		ND*	2.3
2.0					60.0		ND	2.3
3.0					22.0		ND	2.3
4.0					0.0		ND	2.3
5.0					.0		ND	2.3
6.0					.0		ND	2.3
7.0					.0		ND	2.3
8.0					.0		ND	2.3
9.0					.0		ND	2.3
10.0					.0		ND	2.3
11.0					.0		ND	2.3
12.0					.0		ND	2.3
(a.2) Methanol:								
0.0				0.0			ND	
0.5				1.82			ND	
1.0				4.04			ND	
2.0				5.48			ND	
3.0				1.01			ND	
4.0				0.0			ND	
5.0				.0			ND	
6.0				.0			ND	
(b.1) Formaldehyde:								
	0.0		1.86	0.0			ND	2.3
	1.0		0.878	.905			ND	2.3
	2.0		.309	1.13			ND	2.3
	3.0		.0831	0.738			ND	2.3
	4.0		.0119	.216			ND	2.3
	5.0		.0	.0			ND	2.3
	6.0		.0	.0			ND	2.3
(b.2) Formaldehyde:								
	0.487		0.309	1.13				
	1.49		.0831	0.738				
	2.49		.0119	.216				
	3.49		.0	.0				
	4.49		.0	.0				
(c) Formic acid:								
		0.0				100.0	ND	2.7
		.294				68.0	ND	2.7
		.412				58.0	ND	2.7
		.588				39.0	ND	2.7
		.882				13.0	ND	2.7
		1.18				0.0	ND	2.7
		1.47				.0	ND	2.7
		1.76				.0	ND	2.7
		2.06				.0	ND	2.7

* Not detected

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table A-1(b.2), which assumed that 4 moles of peroxide were consumed per mole of methanol. These data show that the quantitative oxidation of formaldehyde occurs at a $[H_2O_2]/[CH_2O]$ ratio of approximately 3 in this experiment, compared with the ratio of 2 shown in equation (A2).

Formic Acid. – The experimental work leading to the acceptance of equation (A3) began with nine 1-liter containers each filled with a liter of deionized water, followed by the addition of 0.20 grams of $FeCl_3 \cdot 6H_2O$ and 0.77 grams of 90-percent formic acid. Less than the traditional 0.2 molar ratio was used to slow the reaction down for more accurate results (if the reaction were to occur too fast there would be some loss of oxidant due to decomposition). Moreover, since the formic acid and ferric chlo-

ride both lower the solution pH, less ferric chloride was chosen to maintain the pH close to the other tests. Increasing ratios of peroxide to formic acid were used. The samples were loosely capped in a hood for 48 hours. The temperature of the solutions varied from approximately 20 to 25 °C. The results of this experimental procedure are shown in table A-1(c) and on figure A-2. These data show that quantitative oxidation of formic acid occurs at a $[H_2O_2]/[CH_2O_2]$ ratio of 1.

Conclusions. – The expected molar ratios (peroxide/organic species) shown in equations (A1) and (A2) were not obtained in these experiments. Therefore, the reactions appear to be either more complex than originally thought, or some peroxide is lost due to decomposition.
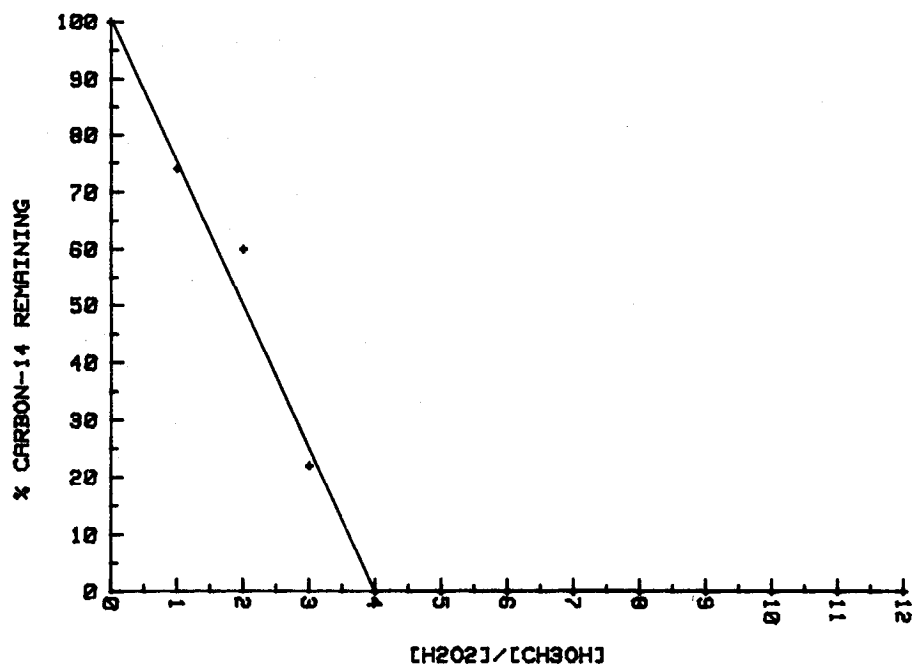
Figure A-1. – Percent ^{14}C remaining as a function of the molar ratio of hydrogen peroxide and methanol.
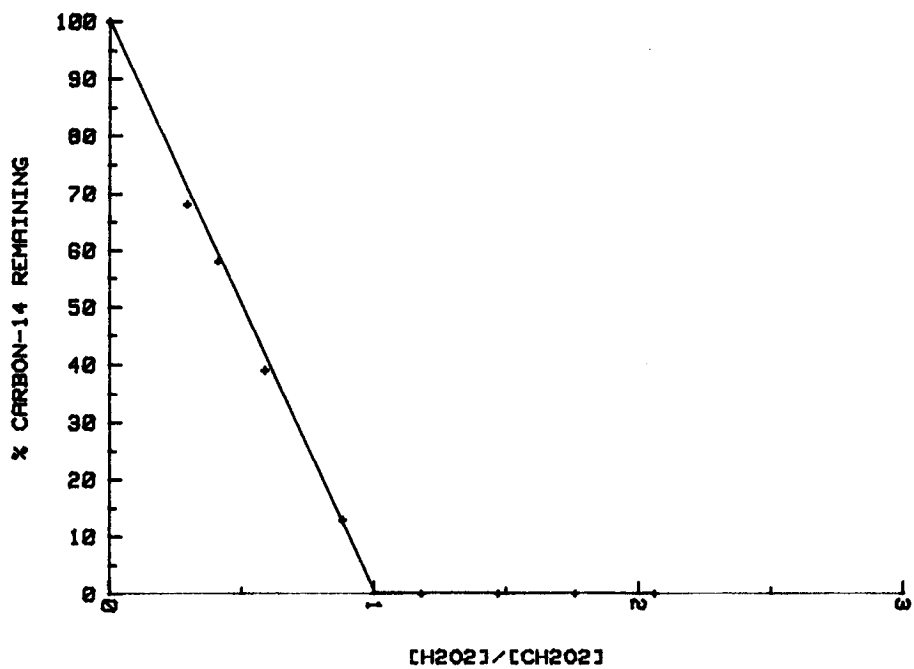
Figure A-2. – Percent ^{14}C remaining as a function of the molar ratio of hydrogen peroxide and formic acid.

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APPENDIX B

TYPICAL DATA PRINTOUT FOR A PILOT-SCALE ADIABATIC TEST

Date	Time	Scan	Chan 12 DEG C	Chan 13 DEG C	Date	Time	Scan	Chan 14 pH	pH

FILE   Data8.   FILE   Data8.
GROUP   1   GROUP   2

First Dat 860324   First Dat 860324
First Tim 103503   First Tim 103507
Interval   1   Interval   1

Date	Time	Scan	Chan 12 DEG C	Chan 13 DEG C	Date	Time	Scan	Chan 14 pH	pH
860324	103503	1	22.6	25.1	860324	103507	1	-0.1411	4.62
860324	103604	2	22.8	25.1	860324	103607	2	-0.1405	4.63
860324	103704	3	22.9	25.0	860324	103707	3	-0.1404	4.63
860324	103804	4	22.8	25.0	860324	103807	4	-0.2642	2.53
860324	103904	5	23.0	25.0	860324	103906	5	-0.2596	2.61
860324	104004	6	23.1	25.0	860324	104006	6	-0.2603	2.60
860324	104104	7	23.2	25.0	860324	104107	7	-0.2619	2.57
860324	104204	8	23.3	25.1	860324	104207	8	-0.2623	2.57
860324	104304	9	23.4	25.1	860324	104307	9	-0.2628	2.56
860324	104404	10	23.4	25.1	860324	104407	10	-0.2631	2.55
860324	104504	11	23.5	25.2	860324	104506	11	-0.2627	2.56
860324	104603	12	23.5	25.2	860324	104606	12	-0.2611	2.59
860324	104704	13	23.5	25.3	860324	104707	13	-0.2636	2.55
860324	104804	14	23.6	25.3	860324	104807	14	-0.2638	2.54
860324	104904	15	23.6	25.4	860324	104907	15	-0.2643	2.54
860324	105004	16	23.7	25.4	860324	105006	16	-0.2645	2.53
860324	105104	17	23.7	25.4	860324	105106	17	-0.2648	2.53
860324	105203	18	23.7	25.5	860324	105206	18	-0.2650	2.53
860324	105304	19	23.7	25.5	860324	105307	19	-0.2652	2.53
860324	105404	20	23.7	25.5	860324	105407	20	-0.2643	2.54
860324	105504	21	23.7	25.6	860324	105506	21	-0.2652	2.53
860324	105604	22	23.8	25.6	860324	105606	22	-0.2656	2.52
860324	105703	23	23.8	25.6	860324	105706	23	-0.2658	2.52
860324	105804	24	23.9	25.7	860324	105807	24	-0.2660	2.51
860324	105904	25	23.9	25.7	860324	105907	25	-0.2662	2.51
860324	110004	26	23.9	25.7	860324	110007	26	-0.2659	2.52
860324	110104	27	24.0	25.8	860324	110106	27	-0.2663	2.51
860324	110204	28	24.0	25.8	860324	110206	28	-0.2664	2.51
860324	110303	29	24.0	25.8	860324	110306	29	-0.2668	2.50
860324	110404	30	24.1	25.9	860324	110407	30	-0.2670	2.50
860324	110504	31	24.1	25.9	860324	110507	31	-0.2671	2.50
860324	110604	32	24.1	25.9	860324	110607	32	-0.2672	2.50
860324	110704	33	24.1	26.0	860324	110706	33	-0.2670	2.50
860324	110804	34	24.1	26.0	860324	110806	34	-0.2674	2.50
860324	110904	35	24.2	26.0	860324	110907	35	-0.2677	2.49
860324	111004	36	24.2	26.1	860324	111007	36	-0.2678	2.49
860324	111104	37	24.2	26.1	860324	111107	37	-0.2679	2.49
860324	111204	38	24.2	26.1	860324	111207	38	-0.2680	2.49
860324	111304	39	24.2	26.1	860324	111306	39	-0.2664	2.51
860324	111403	40	24.2	26.1	860324	111406	40	-0.2681	2.49

Date	Time	Scan	Chan 12 DEG C	Chan 13 DEG C	Date	Time	Scan	Chan 14 pH	pH
860324	111504	41	24.2	26.2	860324	111507	41	-0.2652	2.53
860324	111604	42	24.2	26.2	860324	111607	42	-0.2679	2.49
860324	111704	43	24.1	26.2	860324	111707	43	-0.2684	2.48
860324	111804	44	24.1	26.3	860324	111807	44	-0.2685	2.48
860324	111904	45	24.2	26.3	860324	111906	45	-0.2686	2.48
860324	112003	46	24.2	26.3	860324	112006	46	-0.2686	2.48
860324	112104	47	24.2	26.4	860324	112107	47	-0.2687	2.48
860324	112204	48	24.2	26.4	860324	112207	48	-0.2688	2.48
860324	112304	49	24.3	26.4	860324	112306	49	-0.2691	2.47
860324	112404	50	24.3	26.5	860324	112406	50	-0.2690	2.48
860324	112503	51	24.3	26.5	860324	112506	51	-0.2691	2.47
860324	112604	52	24.3	26.5	860324	112607	52	-0.2691	2.47
860324	112704	53	24.3	26.6	860324	112707	53	-0.2692	2.47
860324	112804	54	24.3	26.6	860324	112807	54	-0.2692	2.47
860324	112904	55	24.4	26.6	860324	112906	55	-0.2691	2.48
860324	113004	56	24.4	26.7	860324	113006	56	-0.2690	2.48
860324	113103	57	24.4	26.7	860324	113106	57	-0.2673	2.51
860324	113204	58	24.4	26.7	860324	113207	58	-0.2688	2.48
860324	113304	59	24.4	26.8	860324	113307	59	-0.2691	2.48
860324	113404	60	24.5	26.8	860324	113407	60	-0.2691	2.48
860324	113504	61	24.5	26.8	860324	113506	61	-0.2691	2.48
860324	113603	62	24.5	26.9	860324	113606	62	-0.2687	2.49
860324	113704	63	24.5	26.9	860324	113707	63	-0.2676	2.50
860324	113804	64	24.5	27.0	860324	113807	64	-0.2688	2.49
860324	113904	65	24.5	27.0	860324	113907	65	-0.2688	2.49
860324	114004	66	24.5	27.0	860324	114007	66	-0.2688	2.49
860324	114104	67	24.5	27.1	860324	114106	67	-0.2686	2.49
860324	114203	68	24.6	27.1	860324	114206	68	-0.2681	2.50
860324	114304	69	24.5	27.2	860324	114307	69	-0.2675	2.51
860324	114404	70	24.6	27.2	860324	114407	70	-0.2683	2.50
860324	114504	71	24.5	27.3	860324	114507	71	-0.2682	2.50
860324	114604	72	24.6	27.3	860324	114607	72	-0.2680	2.51
860324	114704	73	24.6	27.4	860324	114706	73	-0.2677	2.51
860324	114804	74	24.6	27.5	860324	114807	74	-0.2673	2.52
860324	114904	75	24.6	27.5	860324	114907	75	-0.2672	2.52
860324	115004	76	24.6	27.6	860324	115007	76	-0.2673	2.52
860324	115104	77	24.6	27.6	860324	115106	77	-0.2670	2.53
860324	115204	78	24.7	27.7	860324	115206	78	-0.2667	2.53
860324	115303	79	24.7	27.8	860324	115306	79	-0.2664	2.54
860324	115404	80	24.7	27.8	860324	115407	80	-0.2659	2.55
860324	115504	81	24.7	27.9	860324	115507	81	-0.2652	2.56
860324	115604	82	24.7	28.0	860324	115607	82	-0.2654	2.56
860324	115704	83	24.7	28.0	860324	115706	83	-0.2650	2.57
860324	115804	84	24.7	28.1	860324	115806	84	-0.2645	2.57
860324	115903	85	24.7	28.1	860324	115906	85	-0.2640	2.58
860324	120004	86	24.7	28.2	860324	120007	86	-0.2631	2.60
860324	120104	87	24.7	28.3	860324	120107	87	-0.2627	2.61
860324	120204	88	24.7	28.3	860324	120207	88	-0.2624	2.61
860324	120304	89	24.7	28.4	860324	120306	89	-0.2618	2.62
860324	120403	90	24.7	28.4	860324	120406	90	-0.2614	2.63
860324	120504	91	24.7	28.4	860324	120507	91	-0.2612	2.64
860324	120604	92	24.7	28.4	860324	120607	92	-0.2607	2.64
860324	120704	93	24.7	28.5	860324	120707	93	-0.2604	2.65

Date	Time	Scan	Chan 12 DEG C	Chan 13 DEG C	Date	Time	Scan	Chan 14 pH	pH
860324	120804	94	24.8	28.5	860324	120807	94	-0.2602	2.65
860324	120904	95	24.7	28.5	860324	120906	95	-0.2600	2.66
860324	121003	96	24.8	28.5	860324	121006	96	-0.2599	2.66
860324	121104	97	24.8	28.6	860324	121107	97	-0.2596	2.66
860324	121204	98	24.8	28.6	860324	121207	98	-0.2596	2.66
860324	121304	99	24.8	28.5	860324	121307	99	-0.2594	2.67
860324	121404	100	24.8	28.6	860324	121407	100	-0.2592	2.67
860324	121504	101	24.8	28.6	860324	121506	101	-0.2593	2.67
860324	121604	102	24.8	28.5	860324	121607	102	-0.2591	2.67
860324	121704	103	24.8	28.5	860324	121707	103	-0.2590	2.67
860324	121804	104	24.8	28.5	860324	121807	104	-0.2586	2.68
860324	121904	105	24.9	28.5	860324	121906	105	-0.2578	2.69
860324	122004	106	24.8	28.5	860324	122006	106	-0.2588	2.68
860324	122103	107	24.8	28.5	860324	122106	107	-0.2588	2.68
860324	122204	108	24.8	28.5	860324	122207	108	-0.2588	2.68
860324	122304	109	24.8	28.5	860324	122307	109	-0.2587	2.68
860324	122404	110	24.8	28.5	860324	122407	110	-0.2585	2.68
860324	122504	111	24.9	28.5	860324	122506	111	-0.2580	2.69
860324	122604	112	24.9	28.5	860324	122606	112	-0.2584	2.68
860324	122703	113	24.9	28.5	860324	122706	113	-0.2584	2.68
860324	122804	114	24.9	28.4	860324	122807	114	-0.2583	2.68
860324	122904	115	24.9	28.4	860324	122907	115	-0.2582	2.68
860324	123004	116	24.9	28.4	860324	123007	116	-0.2582	2.69
860324	123104	117	24.9	28.4	860324	123106	117	-0.2583	2.68
860324	123203	118	24.8	28.4	860324	123206	118	-0.2583	2.68
860324	123304	119	24.8	28.4	860324	123307	119	-0.2585	2.68
860324	123404	120	24.7	28.4	860324	123407	120	-0.2585	2.68
860324	123504	121	24.6	28.4	860324	123507	121	-0.2585	2.68
860324	123604	122	24.6	28.4	860324	123607	122	-0.2582	2.69
860324	123704	123	24.5	28.4	860324	123706	123	-0.2581	2.69
860324	123803	124	24.5	28.4	860324	123806	124	-0.2584	2.68
860324	123904	125	24.4	28.4	860324	123907	125	-0.2583	2.68
860324	124004	126	24.4	28.4	860324	124007	126	-0.2583	2.68
860324	124104	127	24.4	28.4	860324	124107	127	-0.2584	2.68
860324	124204	128	24.4	28.4	860324	124206	128	-0.2582	2.68
860324	124304	129	24.4	28.4	860324	124306	129	-0.2573	2.70
860324	124404	130	24.3	28.3	860324	124407	130	-0.2581	2.69
860324	124504	131	24.3	28.3	860324	124507	131	-0.2582	2.68
860324	124604	132	24.2	28.3	860324	124607	132	-0.2581	2.69
860324	124704	133	24.2	28.3	860324	124706	133	-0.2581	2.68
860324	124804	134	24.2	28.3	860324	124806	134	-0.2580	2.69
860324	124903	135	24.2	28.3	860324	124906	135	-0.2571	2.70
860324	125004	136	24.2	28.3	860324	125007	136	-0.2578	2.69
860324	125104	137	24.2	28.3	860324	125107	137	-0.2580	2.69
860324	125204	138	24.2	28.3	860324	125207	138	-0.2578	2.69
860324	125304	139	24.1	28.3	860324	125306	139	-0.2578	2.69
860324	125404	140	24.1	28.2	860324	125406	140	-0.2577	2.69
860324	125504	141	24.2	28.2	860324	125507	141	-0.2577	2.69
860324	125604	142	24.2	28.2	860324	125607	142	-0.2577	2.69
860324	125704	143	24.1	28.2	860324	125707	143	-0.2579	2.69
860324	125804	144	24.1	28.2	860324	125807	144	-0.2579	2.69
860324	125904	145	24.2	28.2	860324	125906	145	-0.2578	2.69
860324	130003	146	24.1	28.1	860324	130006	146	-0.2578	2.69

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Date	Time	Scan	Chan 12 DEG C	Chan 13 DEG C	Date	Time	Scan	Chan 14 pH	pH
860324	130104	147	24.2	28.1	860324	130107	147	-0.2570	2.70
860324	130204	148	24.2	28.1	860324	130207	148	-0.2575	2.69
860324	130304	149	24.1	28.1	860324	130307	149	-0.2576	2.69
860324	130404	150	24.1	28.0	860324	130407	150	-0.2577	2.69
860324	130504	151	24.1	28.0	860324	130506	151	-0.2576	2.69
860324	130603	152	24.1	28.0	860324	130606	152	-0.2576	2.69
860324	130704	153	24.1	28.0	860324	130707	153	-0.2570	2.70
860324	130804	154	24.1	28.0	860324	130807	154	-0.2577	2.69
860324	130904	155	24.1	27.9	860324	130907	155	-0.2577	2.69
860324	131004	156	24.1	27.9	860324	131006	156	-0.2577	2.69
860324	131103	157	24.1	27.9	860324	131106	157	-0.2578	2.68
860324	131204	158	24.1	27.9	860324	131207	158	-0.2577	2.69
860324	131304	159	24.1	27.9	860324	131307	159	-0.2577	2.68
860324	131404	160	24.1	27.9	860324	131407	160	-0.2578	2.68
860324	131504	161	24.1	27.8	860324	131506	161	-0.2577	2.68
860324	131604	162	24.1	27.8	860324	131606	162	-0.2577	2.68
860324	131703	163	24.1	27.8	860324	131706	163	-0.2555	2.72
860324	131804	164	24.1	27.8	860324	131807	164	-0.2575	2.69
860324	131904	165	24.1	27.8	860324	131907	165	-0.2571	2.69
860324	132004	166	24.0	27.8	860324	132007	166	-0.2575	2.69
860324	132104	167	24.0	27.7	860324	132106	167	-0.2574	2.69
860324	132204	168	24.0	27.7	860324	132206	168	-0.2574	2.69
860324	132304	169	24.0	27.7	860324	132307	169	-0.2573	2.69
860324	132404	170	23.9	27.7	860324	132407	170	-0.2574	2.69
860324	132504	171	24.0	27.7	860324	132507	171	-0.2569	2.70
860324	132604	172	24.0	27.7	860324	132607	172	-0.2572	2.69
860324	132704	173	24.0	27.7	860324	132706	173	-0.2572	2.69
860324	132803	174	24.1	27.7	860324	132806	174	-0.2572	2.69
860324	132904	175	24.1	27.6	860324	132907	175	-0.2556	2.72
860324	133004	176	24.2	27.6	860324	133007	176	-0.2569	2.69
860324	133104	177	24.2	27.6	860324	133107	177	-0.2571	2.69
860324	133204	178	24.3	27.6	860324	133207	178	-0.2572	2.69
860324	133304	179	24.3	27.5	860324	133306	179	-0.2572	2.69
860324	133403	180	24.4	27.5	860324	133406	180	-0.2575	2.68
860324	133504	181	24.4	27.5	860324	133507	181	-0.2561	2.71
860324	133604	182	24.4	27.5	860324	133607	182	-0.2574	2.68
860324	133704	183	24.5	27.4	860324	193706	183	-0.2566	2.70
860324	133804	184	24.5	27.4	860324	133806	184	-0.2573	2.69
860324	133903	185	24.5	27.4	860324	133906	185	-0.2573	2.69
860324	134004	186	24.5	27.4	860324	134007	186	-0.2573	2.68
860324	134104	187	24.5	27.4	860324	134107	187	-0.2561	2.71
860324	134204	188	24.6	27.4	860324	134207	188	-0.2571	2.69
860324	134304	189	24.6	27.4	860324	134306	189	-0.2571	2.69
860324	134404	190	24.6	27.3	860324	134406	190	-0.2572	2.69
860324	134503	191	24.6	27.3	860324	134506	191	-0.2573	2.68
860324	134604	192	24.6	27.3	860324	134607	192	-0.2573	2.68
860324	134704	193	24.6	27.3	860324	134707	193	-0.2557	2.71
860324	134804	194	24.6	27.3	860324	134807	194	-0.2570	2.69
860324	134904	195	24.6	27.3	860324	134906	195	-0.2573	2.68
860324	135004	196	24.7	27.2	860324	135006	196	-0.2573	2.68
860324	135104	197	24.7	27.2	860324	135107	197	-0.2572	2.68
860324	135204	198	24.7	27.2	860324	135207	198	-0.2572	2.68
860324	135304	199	24.7	27.2	860324	135307	199	-0.2564	2.70

Date	Time	Scan	Chan 12 DEG C	Chan 13 DEG C	Date	Time	Scan	Chan 14 pH	pH
860324	135404	200	24.8	27.2	860324	135407	200	-0.2571	2.69
860324	135504	201	24.8	27.2	860324	135506	201	-0.2572	2.68
860324	135603	202	24.8	27.2	860324	135606	202	-0.2572	2.68
860324	135704	203	24.8	27.1	860324	135707	203	-0.2573	2.68
860324	135804	204	24.8	27.1	860324	135807	204	-0.2573	2.68
860324	135904	205	24.8	27.1	860324	135907	205	-0.2543	2.73
860324	140004	206	24.8	27.1	860324	140007	206	-0.2569	2.69

APPENDIX C
PHASE II ISOTHERMAL TEST DATA

SAMPLE NUMBER	TIME min	pH	TEMP deg C	Fe mmolar	H2O2 value mmolar	H2O2 error mmolar	CH3OH mmolar	CH2O value mmolar	CH2O error mmolar	CH2O2 value mmolar	CH2O2 error mmolar	TEST CONDITIONS
0011	0.0	3.01	35.0	1.020	10.3000	0.250	0.2900	1.8700	0.0679	0.0786	0.0457	EXCESS PEROXIDE
0012	3.2	3.00	35.0		9.5400			1.8000		0.1630		High pH
0013	8.0	2.99	35.0		9.5300			1.6900		0.2580		High temperature
0014	16.0	3.08	35.0		9.2700			1.5800		0.3730		
0015	78.0	3.06	35.3		7.8100			1.1700		0.7370		
0016	383.0	3.03	35.3		4.1000			0.7180		0.9990		
0021	0.0	3.03	15.8	1.060	10.3000	0.250	0.2900	1.9600	0.0685	0.0667	0.0461	EXCESS PEROXIDE
0022	20.4	3.06	15.8		9.8500			1.7800		0.2480		High pH
0023	51.0	3.06	15.8		9.4400			1.5900		0.4530		Low temperature
0024	101.9	3.05	15.6		9.0300			1.3300		0.6720		
0025	499.0	2.98	15.6		4.6600			-9.9900		0.0000		
0026	2558.0	2.88	15.6		0.2680			0.0210		0.0000		
0031	0.0	2.47	34.7	1.150	10.3000	0.250	0.2900	1.8000	0.0689	0.0689	0.0464	EXCESS PEROXIDE
0032	3.2	2.47	34.7		10.3000			1.8100		0.1970		Low pH
0033	8.0	2.47	34.7		9.6500			1.6700		0.3570		High temperature
0034	16.0	2.41	34.7		9.0600			1.4300		0.5750		
0035	78.0	2.47	34.9		4.0700			0.4370		1.3600		
0036	399.0	2.50	35.2		0.0000			0.1070		1.0100		
0041	0.0	2.34	14.9	0.990	10.3000	0.250	0.2900	1.8300	0.0694	0.1380	0.0467	EXCESS PEROXIDE
0042	20.4	2.33	14.9		9.9000			1.8100		0.1970		Low pH
0043	51.0	2.34	15.0		9.6000			1.7500		0.2920		Low temperature
0044	105.0	2.36	15.0		9.5600			1.7400		0.3060		
0045	502.0	2.35	15.6		7.5200			1.1200		0.9950		
0046	2528.0	2.35	16.0		0.7700			0.2700		1.3910		
0051	0.0	2.78	24.6	2.580	34.3000	0.250	0.2900	1.8600	0.0686	0.1830	0.0462	EXCESS PEROXIDE
0052	2.7	2.79	24.6		31.7000			1.5700		0.5830		High catalyst
0053	6.7	2.78	24.6		31.7000			1.3000		0.9080		High peroxide
0054	13.4	2.78	24.7		27.1000			0.7700		1.2200		
0055	65.0	2.77	24.7		3.8300			0.0000		0.0260		
0056	326.0	2.83	24.7		0.0000			0.0000		0.0000		
0061	0.0	2.78	25.0	2.780	3.4300	0.250	0.2900	1.7200	0.0683	0.3020	0.0460	EXCESS FORMALDEHY
0062	59.7	2.73	25.2		1.6400			1.1000		0.8310		High catalyst
0063	149.3	2.68	25.1		0.6600			0.6700		0.7980		Low peroxide
0064	298.7	2.62	25.0		0.0000			0.8400		0.9810		
0065	1453.6	2.49	25.0		0.0000			0.9000		1.0270		
0066	7268.0	2.41	25.0		0.0000			0.8200		1.0230		
0071	0.0	2.77	24.9	0.230	34.3000	0.250	0.2900	1.6600	0.0674	0.0000	0.0454	EXCESS PEROXIDE
0072	2.7	2.78	24.9		32.5000			0.8540		0.0285		Low catalyst
0073	6.7	2.79	24.9		32.5000			0.5950		0.0762		High peroxide
0074	13.4	2.80	25.0		32.5000			0.3740		0.1190		
0075	65.0	2.81	25.0		31.3000			-9.9900		0.6520		
0076	324.8	2.79	24.9		21.1000			0.1180		0.9730		
0081	0.0	2.74	25.1	0.390	3.4300	0.250	0.2900	2.0300	0.0684	0.0000	0.0461	EXCESS FORMALDEHY
0082	59.7	2.73	25.4		3.4400			1.9400		0.1390		Low catalyst
0083	149.3	2.77	25.5		3.2900			1.7900		0.3230		Low peroxode
0084	298.7	2.76	25.5		2.7800			1.6100		0.5960		
0085	1453.6	2.73	25.3		0.7600			0.8230		1.2100		
0086	7407.0	2.55	25.2		0.0000			-9.9900		-9.9900		

SAMPLE NUMBER	TIME min	pH	TEMP deg C	Fe mmolar	H2O2 value mmolar	H2O2 error mmolar	CH3OH mmolar	CH2O value mmolar	CH2O error mmolar	CH2O2 value mmolar	CH2O2 error mmolar	TEST CONDITIONS
0091	0.0	2.74	35.2	1.140	10.3000	0.250	2.9500	19.8000	0.6656	0.0000	0.4482	EXCESS FORMALDEHY
0092	2.5	2.73	35.2		8.8300			22.3000		0.5540		High temperature
0093	6.1	2.73	35.2		8.6800			19.9000		1.4300		High formaldehyde
0094	12.2	2.73	35.2		8.0500			-9.9900		-9.9900		
0095	59.5	2.69	35.5		4.0800			14.6000		5.0300		
0096	297.2	2.66	35.5		0.2590			8.9800		5.4100		
0101	0.0	2.86	35.0	0.860	10.3000	0.250						ZERO ORGANIC
0102	24.4	2.89	35.2		8.9800							High temperature
0103	61.1	2.91	34.5		7.6300							Zero formaldehyde
0104	122.2	2.83	35.0		6.0100							
0105	594.5	2.87	35.1		1.5600							
0106	2972.3	3.05	35.6		0.0000							
0111	0.0	2.75	15.5	1.060	10.3000	0.250	2.9500	19.5000	0.7032	0.0000	0.4736	EXCESS FORMALDEHY
0112	15.6	2.79	15.4		9.0800			18.0300		0.0000		Low temperature
0113	39.5	2.81	15.3		8.8400			19.1500		0.4920		High formaldehyde
0114	77.7	2.82	15.3		8.5300			18.5800		1.1000		
0115	380.0	2.81	15.4		5.7400			15.0500		3.9600		
0116	1728.0	2.71	16.5		0.5220			15.1900		9.5740		
0121	0.0	2.75	15.4	1.11	10.3000	0.250						ZERO ORGANIC
0122	155.4	2.89	15.1		3.1400							Low temperature
0123	412.0	2.89	15.2		1.4000							Zero formaldehyde
0124	777.1	2.89	15.2		0.6600							
0125	3782.0	2.68	17.9		0.0000							
0126	18910.0	-9.99	-9.9		-9.9900							
0131	0.0	2.99	25.7	3.220	10.3000	0.250	0.2900	1.7600	0.0684	0.2180	0.0461	EXCESS PEROXIDE
0132	7.8	2.94	25.6		9.3500			1.4800		0.4820		High pH
0133	19.6	2.91	25.5		8.4100			1.2600		0.6860		High catalyst
0134	39.2	2.90	25.5		7.3700			1.0000		0.8440		
0135	194.0	2.77	25.6		3.2100			0.4550		1.0100		
0136	961.0	2.75	25.2		0.2600			0.2070		0.7920		
0141	0.0	3.00	24.8	0.290	10.3000	0.250	0.2900	2.2000	0.0696	0.0000	0.0469	EXCESS PEROXIDE
0142	7.8	3.00	24.8		10.1000			2.1900		0.0780		High pH
0143	19.6	3.00	24.8		9.8600			2.1200		0.1760		Low catalyst
0144	39.2	3.00	24.9		9.7700			2.0200		0.3590		
0145	193.0	2.96	25.1		7.5600			1.1600		1.1800		
0146	1248.0	2.94	24.9		0.4250			0.0650		0.0000		
0151	0.0	2.50	25.4	3.095	10.3000	0.250	0.2900	1.8300	0.0666	0.2990	0.0448	EXCESS PEROXIDE
0152	7.8	2.50	25.4		9.2300			1.3100		0.5270		Low pH
0153	19.6	2.49	25.5		8.1200			1.3600		0.8390		High catalyst
0154	39.2	2.48	25.5		6.3200			1.0300		1.1200		
0155	191.0	2.57	25.8		0.8000			0.3280		1.2200		
0156	953.3	2.57	25.5		0.0000			0.2630		1.0500		
0161	0.0	2.51	24.5	0.188	10.3000	0.250	0.2900	1.9300	0.0688	0.0000	0.0463	EXCESS PEROXIDE
0162	7.8	2.53	24.5		9.9500			1.8500		0.0406		Low pH
0163	19.6	2.54	24.5		9.7600			1.5000		0.1090		Low catalyst
0164	39.2	2.52	24.5		9.7300			1.3600		0.7410		
0165	190.7	2.53	24.6		8.8400			1.3600		0.7300		
0166	1037.0	2.54	24.5		2.7900			0.1480		1.2100		

SAMPLE NUMBER	TIME min	pH	TEMP deg C	Fe mmolar	H2O2 value mmolar	H2O2 error mmolar	CH3OH mmolar	CH2O value mmolar	CH2O error mmolar	CH2O2 value mmolar	CH2O2 error mmolar	TEST CONDITIONS
0171	0.0	2.75	25.1	1.100	34.3000	0.250	2.9500	20.1800	0.6754	0.0000	0.4548	EXCESS FORMALDEHY
0172	6.0	2.80	25.1		25.8000			19.7900		0.7500		High peroxide
0173	14.9	2.82	25.2		24.8000			18.5000		1.9300		High formaldehyde
0174	29.9	2.82	25.2		23.8000			17.3800		3.5900		
0175	145.4	2.75	25.5		15.8000			11.3400		10.8200		
0176	681.0	2.69	25.7		2.2900			3.8600		15.5500		
0181	0.0	2.76	25.0	1.030	34.3000	0.250						ZERO ORGANIC
0182	59.7	2.75	25.5		14.7000							High peroxide
0183	149.3	2.73	25.5		4.6900							Zero formaldehyde
0184	308.0	2.74	25.6		1.2200							
0185	1453.6	2.71	25.3		0.0000							
0186	7268.0	-9.99	-9.9		-9.9900							
0191	0.0	2.76	24.6	1.160	3.4300	0.250	2.9500	20.0000	0.0678	0.0000	0.0457	EXCESS FORMALDEHY
0192	6.0	2.80	24.6		3.2000			-9.9900		-9.9900		Low peroxide
0193	14.9	2.83	24.6		2.9300			20.7810	0.6577	0.1930	0.4429	High formaldehyde
0194	29.9	2.85	24.8		2.7800			21.0750		0.4150		
0195	145.4	2.83	25.0		1.5300			18.2450		1.6060		
0196	733.0	2.84	25.1		0.0000			18.5100		2.7760		
0201	0.0	2.74	25.5	0.851	3.4300	0.250						ZERO ORGANIC
0202	59.7	2.75	25.6		2.7400							Low peroxide
0203	149.3	2.81	25.6		1.8400							Zero formaldehyde
0204	298.7	2.81	25.6		1.1300							
0205	1453.6	2.80	25.5		0.1400							
0206	7295.0	2.71	25.1		0.0000							
0211	0.0	2.73	25.2	0.859	10.3000	0.250	0.2900	1.9800	0.0684	0.0736	0.0460	EXCESS PEROXIDE
0212	7.8	2.74	25.2		9.9700			1.9100		0.0247		
0213	19.6	2.73	25.2		9.7000			1.7900		0.4280		
0214	39.2	2.73	25.2		9.1000			1.5500		0.6920		
0215	190.7	2.68	25.8		3.8900			0.2830		1.2300		
0216	1045.0	2.69	25.5		0.0000			0.0316		0.4120		
0221	0.0	2.75	25.1	1.130	10.3000	0.250	0.2900	1.7700	0.0702	0.0570	0.0473	EXCESS PEROXIDE
0222	7.8	2.74	25.1		9.8500			1.6900		0.1910		
0223	19.6	2.75	25.1		9.2900			1.5800		0.3910		
0224	39.2	2.74	25.1		8.6000			1.3400		0.6650		
0225	208.0	2.73	25.1		2.6900			0.1800		0.8330		
0226	1110.0	2.71	25.2		0.0000			0.0700		0.2850		
0231	0.0	2.75	24.8	1.070	10.3000	0.250	0.2900	2.1300	0.0686	0.0564	0.0462	EXCESS PEROXIDE
0232	7.8	2.75	24.8		10.2000			2.0300		0.2320		
0233	19.6	2.75	24.8		9.5500			1.8600		0.4400		
0234	39.2	2.74	24.8		9.0900			1.6400		0.7490		
0235	196.0	2.77	25.1		3.2300			0.2500		0.9470		
0236	1250.0	2.72	25.0		0.0000			0.0600		0.1990		
0241	0.0	2.74	34.7	3.370	10.3000	0.250	0.2900	1.7700	0.0686	0.3460	0.0462	EXCESS PEROXIDE
0242	3.2	2.73	34.8		9.6300			-9.9900		0.3760		High temperature
0243	8.0	2.72	34.8		8.6100			1.1600		0.8790		High catalyst
0244	16.0	2.71	34.9		7.3500			0.8470		1.0400		
0245	78.0	2.66	35.3		2.4700			0.2370		0.9100		
0246	395.0	2.60	35.4		0.0000			-9.9900		0.9030		

SAMPLE NUMBER	TIME min	pH	TEMP deg C	Fe mmolar	H2O2 value mmolar	H2O2 error mmolar	CH3OH mmolar	CH2O value mmolar	CH2O error mmolar	CH2O2 value mmolar	CH2O2 error mmolar	TEST CONDITIONS
0251	0.0	2.76	34.4	0.270	10.3000	0.250	0.2900	1.9500	0.0685	0.0000	0.0462	EXCESS PEROXIDE
0252	3.2	2.78	34.4		10.4000			1.9000		0.0393		High temperature
0253	8.0	2.79	34.4		10.2000			1.8700		0.0941		Low catalyst
0254	16.0	2.78	34.5		10.1000			1.8500		0.1880		
0255	80.0	2.78	34.8		8.5500			1.2200		0.7930		
0256	411.0	2.81	35.2		2.1800			0.0754		0.7390		
0261	0.0	2.75	15.9	3.110	10.3000	0.250	0.2900	1.8200	0.0690	0.1550	0.0465	EXCESS PEROXIDE
0262	20.4	2.76	15.9		9.3800			1.5800		0.4580		Low temperature
0263	51.0	2.77	15.9		8.2000			1.2500		0.7750		High catalyst
0264	101.9	2.76	15.7		6.6300			0.8140		1.0200		
0265	496.1	2.73	15.7		0.9810			0.1080		0.4910		
0266	2558.0	2.63	15.8		0.0000			0.0776		0.3310		
0271	0.0	2.58	14.9	0.290	10.3000	0.250	0.2900	1.8900	0.0689	0.0000	0.0464	EXCESS PEROXIDE
0272	20.4	2.58	15.0		10.5300			1.9000		0.0520		Low temperature
0273	51.0	2.58	15.0		10.1500			1.7900		0.1140		Low catalyst
0274	101.9	2.59	15.1		9.9200			1.8500		0.1880		
0275	496.1	2.56	15.6		9.0900			1.3400		0.7350		
0276	2523.0	2.54	16.1		2.4300			0.1400		1.2080		
0281	0.0	3.02	25.0	1.090	34.3000	0.250	0.2900	1.7800	0.0678	0.0429	0.0456	EXCESS PEROXIDE
0282	2.7	3.02	25.0		32.3000			1.6900		0.1710		High pH
0283	6.7	3.02	25.0		31.7000			1.5800		0.3090		High peroxide
0284	13.4	3.01	25.0		31.0000			1.3900		0.5150		
0285	65.0	2.99	25.1		26.8000			0.3120		1.1100		
0286	324.8	2.90	24.9		12.6000			0.0185		0.1420		
0291	0.0	2.97	25.4	0.913	3.4300	0.250	0.2900	1.5100	0.0685	0.0780	0.0461	EXCESS FORMALDEHY
0292	59.7	2.97	25.5		2.9600			1.3900		0.3180		High pH
0293	149.3	2.95	25.5		2.2400			1.2500		0.5160		Low peroxide
0294	298.7	2.96	25.5		1.5400			1.0800		0.6800		
0295	1453.6	2.90	25.4		0.2600			0.8100		1.1200		
0296	7283.0	2.83	25.1		0.0000			0.7720		1.1200		
0301	0.0	2.54	24.6	1.013	34.3000	0.250	0.2900	2.0000	0.0684	0.0726	0.0461	EXCESS PEROXIDE
0302	2.7	2.55	24.6		32.7000			1.9700		0.2150		Low pH
0303	6.7	2.55	24.6		32.4000			1.6500		0.3110		High peroxide
0304	13.4	2.54	24.7		31.5000			1.7100		0.5430		
0305	65.0	2.56	24.8		25.1000			0.5600		1.5400		
0306	328.0	2.60	24.7		1.4700			0.0000		0.0840		
0311	0.0	2.50	25.1	1.030	3.4300	0.250	0.2900	1.7500	0.0695	0.1140	0.0468	EXCESS FORMALDEHY
0312	59.7	2.50	25.4		2.7100			1.6700		0.4030		Low pH
0313	149.3	2.46	25.5		-9.9900			-9.9900		-9.9900		Low peroxide
0314	299.0	2.53	25.6		1.0900			1.1800		0.9530		
0315	1453.6	2.44	25.3		0.0000			0.9330		1.1100		
0316	7268.0	2.36	25.0		0.0000			0.8530		1.0700		
0321	0.0	2.73	24.6	3.220	10.3000	0.250	2.9500	19.8000	0.0667	0.0000	0.0449	EXCESS FORMALDEHY
0322	6.0	2.76	24.7		8.6500			18.4800	0.6487	0.9300	0.4369	High catalyst
0323	14.9	2.75	24.7		7.8200			19.0000		1.8900		High formaldehyde
0324	29.9	2.74	24.7		7.0300			16.6600		2.9100		
0325	145.4	2.67	24.9		2.2900			13.0200		5.9300		
0326	726.8	2.62	25.1		0.0000			13.6400		7.7100		

SAMPLE NUMBER	TIME min	pH	TEMP deg C	Fe mmolar	H2O2 value mmolar	H2O2 error mmolar	CH3OH mmolar	CH2O value mmolar	CH2O error mmolar	CH2O2 value mmolar	CH2O2 error mmolar	TEST CONDITIONS
0331	0.0	2.76	25.0	3.130	10.3000	0.250						ZERO ORGANIC
0332	59.7	2.71	25.2		1.7800							High catalyst
0333	149.3	2.66	25.2		0.5200							Zero formaldehyde
0334	301.0	2.56	25.4		0.2700							
0335	1453.6	2.48	24.9		0.0000							
0336	7268.0	-9.99	-9.9		-9.9900							
0341	0.0	2.75	24.8	0.320	10.3000	0.250	2.9500	22.5000	0.6885	0.0000	0.4637	EXCESS FORMALDEHY
0342	6.0	2.74	24.7		9.0000			21.7000		0.0000		Low catalyst
0343	14.9	2.76	24.7		8.6900			20.5000		0.0000		High formaldehyde
0344	29.9	2.76	24.7		8.9000			-9.9900		-9.9900		
0345	145.4	2.74	24.8		7.9200			21.1000		0.0000		
0346	730.0	2.75	25.2		2.4900			15.2000		7.9200		
0351	0.0	2.75	25.1	0.200	10.3000	0.250						ZERO ORGANIC
0352	59.7	2.76	25.3		9.6600							Low catalyst
0353	149.3	2.77	25.3		8.1400							Zero formaldehyde
0354	294.0	2.73	25.4		5.6600							
0355	1453.6	2.76	24.9		0.7600							
0356	2826.0	2.75	24.9		0.0000							
0361	0.0	3.00	24.9	1.110	10.3000	0.250	2.9500	20.1000	0.6215	0.0000	0.4185	EXCESS FORMALDEHY
0362	6.0	3.02	24.7		8.8900			-9.9900		-9.9900		High pH
0363	14.9	3.01	24.7		8.1800			19.6000		-9.9900		High formaldehyde
0364	29.9	2.99	24.7		7.9500			18.2000		-9.9900		
0365	145.4	2.90	24.9		4.3300			-9.9900		-9.9900		
0366	726.8	2.79	25.2		0.2750			11.7000		-9.9900		
0371	0.0	3.00	25.1	0.990	10.3000	0.250						ZERO ORGANIC
0372	59.7	2.99	25.2		7.3700							High pH
0373	149.3	2.97	25.1		4.9600							Zero formaldehyde
0374	298.7	2.96	25.0		2.8500							
0375	1453.6	2.88	25.0		0.2500							
0376	7268.0	2.77	24.9		0.0000							
0381	0.0	2.50	25.0	1.090	10.3000	0.250	2.9500	19.3900	0.6658	0.0000	0.4484	EXCESS PEROXIDE
0382	6.0	2.50	25.0		9.4600			19.4800		0.0000		Low pH
0383	14.9	2.50	25.0		8.9500			19.2400		0.3990		High formaldehyde
0384	29.9	2.50	25.1		8.9500			18.7300		0.9170		
0385	145.4	2.49	25.4		5.6100			17.4700		4.4590		
0386	733.0	2.45	26.2		0.4400			15.3200		9.4250		
0391	0.0	2.50	25.0	1.180	10.3000	0.250						ZERO ORGANIC
0392	59.7	2.48	25.4		5.1200							Low pH
0393	149.3	2.52	25.5		2.5500							Zero formaldehyde
0394	298.7	2.52	25.5		1.4000							
0395	1453.6	2.49	25.2		0.0000							
0396	7268.0	-9.99	-9.9		-9.9900							
0401	0.0	2.87	35.2	1.000	34.3000	0.250	0.2900	1.8900	0.0678	0.0735	0.0457	EXCESS PEROXIDE
0402	1.1	2.87	35.2		32.6000			1.7800		0.1790		High temperature
0403	2.7	2.86	35.2		32.4000			1.6900		0.3210		High peroxide
0404	5.5	2.85	35.2		31.7000			1.2000		0.3870		
0405	26.6	2.87	35.3		26.9000			0.3480		0.6150		
0406	132.8	2.86	35.3		6.6200			0.0000		0.0249		

SAMPLE NUMBER	TIME min	pH	TEMP deg C	Fe mmolar	H2O2 value mmolar	error mmolar	CH3OH mmolar	CH2O value mmolar	error mmolar	CH2O2 value mmolar	error mmolar	TEST CONDITIONS
0411	0.0	2.88	34.8	0.840	3.4300	0.250	0.2900	1.9800	0.0683	0.0694	0.0460	EXCESS FORMALDEHY
0412	24.4	2.85	35.2		2.6900			1.7500		0.3390		High temperature
0413	61.1	2.91	34.6		2.2400			1.5500		0.5640		Low peroxide
0414	122.2	2.86	35.0		1.5800			1.3500		0.7600		
0415	594.5	2.85	35.1		0.2620			-9.9900		-9.9900		
0416	2972.3	3.04	35.6		0.0000			0.7560		1.1200		
0421	0.0	2.75	15.8	1.080	34.3000	0.250	0.2900	1.8400	0.0687	0.1220	0.0463	EXCESS PEROXIDE
0422	7.0	2.77	15.8		28.0000			1.7500		0.1960		Low temperature
0423	17.4	2.78	15.8		27.8000			1.7100		0.3420		High peroxide
0424	34.7	2.80	15.7		27.5000			1.5000		0.5320		
0425	169.0	2.81	15.5		22.7000			-9.9900		0.0316		
0426	816.0	2.84	15.6		1.0900			0.0252		0.0000		
0431	0.0	2.75	15.5	1.220	3.4300	0.250	0.2900	1.9300	0.0682	0.1270	0.0459	EXCESS FORMALDEHY
0432	155.4	2.81	15.3		3.2100			1.6700		0.4550		Low temperature
0433	404.0	2.79	15.6		2.1300			1.4100		0.7250		Low peroxide
0434	777.1	2.79	15.5		1.5800			1.1400		0.9620		
0435	3782.0	2.60	18.3		0.0000			0.7310		1.1000		
0436	18910.0	-9.99	-9.9		-9.9900			-9.9900		-9.9900		
0441	0.0	2.75	25.2	1.450	10.3000	0.250	0.2900	1.9300	0.0691	0.0820	0.0466	EXCESS PEROXIDE
0442	7.8	2.76	25.2		10.0000			1.7900		0.2280		
0443	19.6	2.76	25.2		9.2400			1.6100		0.4400		
0444	39.2	2.76	25.2		8.4700			1.3300		0.7300		
0445	192.0	2.76	25.4		2.5800			0.1200		0.7100		
0446	1110.0	2.70	25.0		0.0000			0.0200		0.1790		
0451	0.0	2.78	25.2	1.029	10.3000	0.250	0.2900	1.8500	0.0683	0.1190	0.0460	EXCESS PEROXIDE
0452	7.8	2.79	25.2		9.8100			-9.9900		0.2460		
0453	19.6	2.79	25.2		9.4200			1.5100		0.4960		
0454	39.2	2.77	25.4		8.5100			1.1900		0.7550		
0455	204.0	2.73	25.5		2.1000			0.0960		0.7800		
0456	966.0	2.72	25.5		0.0000			0.0107		0.2400		
0461	0.0	2.76	24.9	1.090	10.3000	0.250	0.2900	1.9700	0.0693	0.0930	0.0467	EXCESS PEROXIDE
0462	7.8	2.75	25.0		9.7400			1.8800		0.2440		
0463	19.6	2.75	25.0		9.4500			1.6800		0.4190		
0464	39.2	2.75	25.1		8.7000			1.4500		0.6900		
0465	190.7	2.72	25.3		3.6100			0.2700		1.0840		
0466	1040.0	2.72	25.0		0.2600			0.0400		0.3570		
0471	0.0	3.27	25.0	1.150	10.3000	0.250	0.2900	1.7400	0.0689	0.0584	0.0464	EXCESS PEROXIDE
0472	7.8	3.21	25.0		10.6000			1.6900		0.1070		High pH
0473	19.6	3.37	25.0		10.5000			1.6600		0.1630		
0474	39.2	3.37	25.0		10.2000			1.5800		0.2240		
0475	196.0	3.28	25.0		9.7000			1.3300		0.5450		
0476	947.0	3.05	25.2		7.6500			0.6890		1.0400		
0481	0.0	2.25	25.5	1.050	10.3000	0.250	0.2900	2.2900	0.0688	0.0527	0.0464	EXCESS PEROXIDE
0482	7.8	2.26	25.4		10.5000			1.9000		0.1420		Low pH
0483	19.6	2.25	25.4		10.0000			1.8000		0.2500		
0484	39.2	2.25	25.4		9.6000			1.6800		0.4060		
0485	207.0	2.30	25.5		5.8400			0.8070		1.0200		
0486	1040.0	2.28	25.0		0.3800			0.3000		1.2900		

SAMPLE NUMBER	TIME min	pH	TEMP deg C	Fe mmolar	H2O2 value mmolar	H2O2 error mmolar	CH3OH mmolar	CH2O value mmolar	CH2O error mmolar	CH2O2 value mmolar	CH2O2 error mmolar	TEST CONDITIONS
0491	0.0	2.74	25.2	1.130	10.3000	0.250	0.2900	2.2000	0.0691	0.0667	0.0465	EXCESS PEROXIDE +
0492	7.8	2.74	25.1		10.1000			2.1740		0.1960		SALT (0.5 mmol/L
0493	19.6	2.74	25.1		9.9100			2.0200		0.3420		Na2SO4)
0494	39.2	2.74	25.2		9.7100			1.8500		0.5690		
0495	191.0	2.75	25.5		6.3200			0.8230		1.2900		
0496	1154.0	2.84	25.5		0.0000			0.0520		0.2270		
0501	0.0	2.71	25.4	1.180	10.3000	0.250	0.2900	1.9100	0.0684	0.1760	0.0461	EXCESS PEROXIDE +
0502	7.8	2.72	25.4		10.5000			1.8700		0.2260		SALT (10.0 mmol/L
0503	19.6	2.72	25.4		10.4000			1.8000		0.3240		Na2SO4)
0504	39.2	2.69	25.4		10.2000			1.5700		0.4630		
0505	199.0	2.80	25.7		8.0600			1.0100		1.0700		
0506	1090.0	2.78	25.4		0.6800			0.0150		0.2070		
0511	0.0	2.74	25.0	1.150	10.3000	0.250	0.2900	1.8200	0.0666	0.8260	0.0449	EXCESS PEROXIDE +
0512	7.8	2.75	25.0		10.1000			1.6900		0.7770		SALT (200. mmol/L
0513	19.6	2.77	25.0		10.1000			1.7100		0.8350		Na2SO4)
0514	39.2	2.78	25.0		10.1000			1.6700		0.8750		
0515	192.0	2.84	24.9		9.2700			1.2300		1.2500		
0516	959.0	2.82	25.1		3.7900			0.1890		1.2100		
0521	0.0	2.78	25.2	1.030	10.3000	0.250	0.2900	1.8500	0.0686	0.1140	0.0462	EXCESS PEROXIDE +
0522	7.8	2.79	25.2		9.8100			1.5400		0.2450		SALT (6.0 MMOL/l
0523	19.6	2.79	25.2		9.2800			1.5300		0.5010		NaCl)
0524	39.2	2.77	25.3		8.4700			1.2200		0.7610		
0525	212.0	2.73	25.4		1.6800			0.1610		0.8070		
0526	968.0	2.69	25.6		0.0000			0.0543		0.4190		
1011	0.0	3.01	25.2	1.140	10.3000	0.250	3.3300	0.0589	0.0686	0.1030	0.0462	EXCESS PEROXIDE
1012	7.8	2.99	25.3		10.2000			0.1290		0.1390		Midpoint methanol
1013	19.6	2.99	25.3		10.2000			0.2270		0.2000		High pH
1014	39.2	2.97	25.2		9.9700			0.3500		0.2810		
1015	193.0	2.88	25.6		7.5900			0.8400		0.7130		
1016	1161.0	2.80	25.4		0.6760			0.3070		1.0200		
1021	0.0	2.51	25.4	1.030	10.3000	0.250	3.3300	0.0472	0.0688	0.0924	0.0463	EXCESS PEROXIDE
1022	7.8	2.51	25.4		10.6000			0.0684		0.1130		Midpoint methonal
1023	19.6	2.52	25.4		10.3000			0.1020		0.1230		Low pH
1024	39.2	2.52	25.4		10.2000			0.1710		0.1750		
1025	201.0	2.54	25.5		8.6200			0.5580		0.4360		
1026	1040.0	2.52	25.0		1.3500			0.4990		1.4700		
1031	0.0	2.76	34.5	1.130	10.3000	0.250	3.3300	0.0000	0.0684	0.0816	0.0460	EXCESS PEROXIDE
1032	3.2	2.77	34.5		11.0000			0.0472		0.0973		Midpoint methanol
1033	8.0	2.76	34.5		10.6000			0.0990		0.1270		High temperature
1034	16.0	2.75	34.6		10.4000			0.1860		0.1680		
1035	78.0	2.71	35.0		8.3000			0.5560		0.5050		
1036	412.0	2.68	34.8		2.0700			0.5140		1.2800		
1041	0.0	2.75	15.3	1.070	10.3000	0.250	3.3300	0.0498	0.0687	0.1070	0.0463	EXCESS PEROXIDE
1042	20.4	2.76	15.3		10.5000			-9.9900		-9.9900		Midpoint methanol
1043	51.0	2.77	15.3		10.2000			0.0826		0.1130		Low temperature
1044	101.9	2.78	15.3		9.9500			0.1330		0.1330		
1045	496.1	2.78	15.5		9.1200			0.4490		0.3650		
1046	2505.0	2.71	17.4		2.0600			0.4150		1.1400		

SAMPLE NUMBER	TIME min	pH	TEMP deg C	Fe mmolar	H2O2 value mmolar	H2O2 error mmolar	CH3OH mmolar	CH2O value mmolar	CH2O error mmolar	CH2O2 value mmolar	CH2O2 error mmolar	TEST CONDITIONS
1051	0.0	2.75	25.6	3.150	10.3000	0.250	3.3300	0.0210	0.0684	0.4420	0.0461	EXCESS PEROXIDE
1052	7.8	2.76	25.5		9.9500			0.1690		0.4890		Midpoint methanol
1053	19.6	2.77	25.5		8.8500			0.3570		0.6130		High catalyst
1054	39.2	2.77	25.5		7.7700			0.5350		0.8120		
1055	217.0	2.62	25.8		2.0500			0.5000		1.1840		
1056	1125.0	2.44	25.2		0.0000			0.3860		1.1060		
1061	0.0	2.75	25.0	0.290	10.3000	0.250	3.3300	0.0210	0.0689	0.0000	0.0464	EXCESS PEROXIDE
1062	7.8	2.74	25.0		10.6600			0.0330		0.0000		Midpoint methanol
1063	19.6	2.74	25.0		10.3900			0.0380		0.0000		Low catalyst
1064	39.2	2.74	25.0		10.5100			-9.9900		-9.9900		
1065	191.0	2.76	25.4		10.0700			0.2290		0.0820		
1066	1040.0	2.72	25.2		7.0500			0.7130		0.7470		
1071	0.0	2.75	24.6	0.735	34.3000	0.250	3.3300	0.0103	0.0679	0.0887	0.0458	EXCESS PEROXIDE
1072	2.7	2.76	24.6		33.6000			0.0359		0.1160		Midpoint methanol
1073	6.7	2.76	24.7		33.7000			0.0615		0.1330		High peroxide
1074	13.4	2.77	24.7		33.3000			0.1080		0.1530		
1075	65.0	2.77	25.0		32.0000			0.3910		0.4610		
1076	324.8	2.79	25.5		13.2000			0.0416		0.4650		
1081	0.0	2.75	25.0	1.130	3.4300	0.250	3.3300	0.0210	0.0686	0.1020	0.0462	EXCESS METHANOL
1082	30.0	2.77	25.2		3.6900			0.0980		0.1290		High methanol
1083	74.9	2.77	25.3		3.3200			0.2110		0.1530		Low peroxide
1084	149.8	2.77	25.4		2.7000			0.4170		0.2270		
1085	745.0	2.66	26.6		1.0300			0.9810		0.6920		
1086	3355.0	2.63	25.5		0.0000			0.7330		1.1000		
1091	0.0	2.75	25.2	2.050	10.3000	0.250	11.1000	0.0103	0.0691	0.1970	0.0465	EXCESS METHANOL
1092	9.0	2.74	25.3		10.4000			0.0521		0.2200		High methanol
1093	22.5	2.73	25.3		10.2000			0.1040		0.2390		
1094	44.9	2.72	25.4		10.1000			0.1200		0.1690		
1095	218.7	2.78	25.6		8.8100			0.7760		0.6400		
1096	1093.5	2.70	25.3		3.3200			1.8200		2.3800		
1101	0.0	2.76	25.2	1.060	10.3000	0.250	1.1100	0.0150	0.0696	0.0000	0.0468	EXCESS PEROXIDE
1102	7.8	2.76	25.1		10.2000			0.0530		0.0210		Low methanol
1103	19.6	2.77	25.2		9.8500			0.0890		0.0420		
1104	39.2	2.77	25.2		9.7500			0.1510		0.0830		
1105	195.0	2.80	25.4		6.6600			-9.9900		-9.9900		
1106	1110.0	2.70	25.5		0.3860			0.0100		0.0000		
1111	0.0	3.24	25.4	1.190	10.3000	0.250	3.3300	0.0000	0.0691	0.1080	0.0465	EXCESS PEROXIDE
1112	7.8	3.23	25.4		10.5000			0.0400		0.1420		Midpoint methanol
1113	19.6	3.22	25.4		9.6200			0.0753		0.1530		High pH
1114	39.2	3.19	25.4		9.0300			0.1110		0.1390		
1115	197.0	3.25	25.7		5.0700			0.2860		0.2620		
1116	1087.0	3.32	25.5		0.7700			0.5250		0.3530		
1121	0.0	2.25	24.5	0.745	10.3000	0.250	3.3300	0.0103	0.0682	0.0788	0.0459	EXCESS PEROXIDE
1122	7.8	2.25	24.5		10.1000			0.0153		0.0887		Midpoint methanol
1123	19.6	2.25	24.5		10.1000			0.0416		0.1150		Low pH
1124	39.2	2.22	24.5		9.9900			0.0832		0.1000		
1125	191.0	2.24	24.6		9.1800			0.3220		0.2450		
1126	1025.0	2.20	24.5		3.9000			0.6620		1.2000		

SAMPLE	TIME	pH	TEMP	Fe	H2O2		CH3OH	CH2O		CH2O2		TEST CONDITIONS
NUMBER	min		deg C	mmolar	value mmolar	error mmolar	mmolar	value mmolar	error mmolar	value mmolar	error mmolar	
1131	0.0	2.74	25.1	1.120	10.3000	0.250	3.3300	0.0320	0.0693	0.0670	0.0467	EXCESS PEROXIDE
1132	7.8	2.74	25.1		10.2400			0.0065		0.0840		Midpoint methanol
1133	19.6	2.74	25.1		9.9500			0.1260		0.1050		
1134	39.2	2.74	25.0		9.9200			0.2190		0.1580		
1135	211.0	2.74	25.1		7.7300			0.6870		0.6130		
1136	1110.0	2.70	25.2		0.2600			0.2580		0.9930		
1141	0.0	2.79	25.6	1.100	10.3000	0.250	3.3300	0.0092	0.0676	0.1140	0.0455	EXCESS PEROXIDE
1142	7.8	2.78	25.5		10.7000			0.0472		0.1120		Midpoint methanol
1143	19.6	2.78	25.5		10.5000			0.1110		0.1530		
1144	39.2	2.79	25.5		10.4000			0.2000		0.2010		
1145	191.0	2.68	25.6		8.0000			0.5620		0.5750		
1146	960.0	2.67	25.2		0.2600			0.1890		0.8910		

Updated 7/16/86 WJB

APPENDIX D

REGRESSION RESULTS OF PHASE II ISOTHERMAL TEST DATA

FORMALDEHYDE OXIDATION: SIMULATION BY GEAR NUMERICAL INTEGRATION

PARAMETER VALUES ESTIMATED FOR THE 16-PARAMETER MODEL:

```
B( 1) =    4.8014
B( 2) =     .5293
B( 3) =   1.0000
B( 4) =     .8046
B( 5) =     .6002
B( 6) =     .4786
B( 7) =   -.0943
B( 8) =  10.7196
B( 9) =     .5293
B(10) =   1.0000
B(11) =     .8046
B(12) =     .6002
B(13) =     .4786
B(14) =   -.0943
B(15) =     .1090
B(16) =  -6.0700
B(17) =   5.8695
B(18) =     .5293
B(19) =   1.0000
B(20) =     .8046
B(21) =     .6002
B(22) =     .4786
B(23) =   -.0943
B(24) =     .1090
B(25) =  -6.0700
B(26) =  10.5603
B(27) =   1.5000
B(28) =   1.2399
B(29) =     .4390
B(30) =   1.1993
B(31) =   -.1750
B(32) =     .1090
B(33) -   -6.0700
B(34) =   -.8810
B(35) =   -.8810
B(36) =   -.8810
B(37) =   1.0000
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CASE NO	OBS NO	TIME [SEC]	HYDROGEN PEROXIDE CONCENTRATION [MILLIMOLAR] OBS	CALC	WEIGHTED RESIDUAL (OBS-CALC)/ACC	METHANOL CONCENTRATION [MILLIMOLAR] CALCULATED	FORMALDEHYDE CONCENTRATION [MILLIMOLAR] OBS	CALC	WEIGHTED RESIDUAL (OBS-CALC)/ACC	FORMIC ACID CONCENTRATION [MILLIMOLAR] OBS	CALC	WEIGHTED RESIDUAL (OBS-CALC)/ACC
TEST NO 1	INITIAL CONDITIONS: PH = 3.01 FECL3, MMOLAR = 1.0 T, C = 35.0 NACL, MMOLAR = 0.0 NA2SO4, MMOLAR = 0.0											
1	1	0	10.300			.290	1.870			.079		
2	2	192	9.540	10.130	-2.36	.274	1.800	1.791	.13	.163	.161	.04
3	3	480	9.530	9.877	-1.39	.252	1.690	1.678	.18	.258	.272	-.31
4	4	960	9.270	9.490	-.88	.219	1.580	1.509	1.05	.373	.425	-1.13
5	5	4680	7.810	7.002	3.23	.061	1.170	.612	8.22	.737	.985	-5.43
6	6	22980	4.100	1.965	8.54	-.000	.718	-.001	10.60	.999	.430	12.45
TEST NO 2	INITIAL CONDITIONS: PH = 3.03 FECL3, MMOLAR = 1.1 T, C = 15.8 NACL, MMOLAR = 0.0 NA2SO4, MMOLAR = 0.0											
7	1	0	10.300			.290	1.960			.067		
8	2	1223	9.850	10.051	-.80	.269	1.780	1.852	-1.05	.248	.179	1.50
9	3	3060	9.440	9.684	-.98	.240	1.590	1.701	-1.62	.453	.324	2.80
10	4	6114	9.030	9.103	-.29	.198	1.330	1.476	-2.12	.672	.518	3.33
11	5	29940	4.660	5.474	-3.26	.031	-9.990	.437	0.00	-9.990	1.069	0.00
12	6	153480	.268	.545	-1.11	-.000	.021	-.006	.39	-9.990	.548	0.00
TEST NO 3	INITIAL CONDITIONS: PH = 2.47 FECL3, MMOLAR = 1.2 T, C = 34.7 NACL, MMOLAR = 0.0 NA2SO4, MMOLAR = 0.0											
13	1	0	10.300			.290	1.800			.069		
14	2	192	10.300	9.990	1.24	.270	1.810	1.704	1.54	.197	.169	.60
15	3	480	9.650	9.540	.44	.243	1.670	1.570	1.45	.357	.299	1.26
16	4	960	9.060	8.862	.79	.206	1.430	1.383	.68	.575	.463	2.42
17	5	4680	4.070	4.866	-3.19	.050	.437	.502	-.95	1.360	.972	8.36
18	6	23940	0.000	.462	-1.85	-.004	.107	.004	1.49	1.010	.733	5.98
TEST NO 4	INITIAL CONDITIONS: PH = 2.34 FECL3, MMOLAR = 1.0 T, C = 14.9 NACL, MMOLAR = 0.0 NA2SO4, MMOLAR = 0.0											
19	1	0	10.300			.290	1.830			.138		
20	2	1223	9.900	9.997	-.39	.275	1.810	1.754	.81	.197	.215	-.39
21	3	3060	9.600	9.545	.22	.252	1.750	1.643	1.54	.292	.320	-.61
22	4	6300	9.560	8.736	3.30	.215	1.740	1.454	4.12	.306	.486	-3.85
23	5	30120	7.520	4.522	11.99	.069	1.120	.645	6.85	.995	.985	.21
24	6	151680	.770	.374	1.58	.001	.270	..097	2.50	1.391	.966	9.09

			HYDROGEN PEROXIDE			METHANOL	FORMALDEHYDE			FORMIC ACID		
			CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL
CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC

TEST NO 5 INITIAL CONDITIONS:
PH = 2.78   FECL3, MMOLAR = 2.6
T, C = 24.6   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
25	1	0	34.300			.290	1.860			.183		
26	2	162	31.700	33.302	-6.41	.244	1.570	1.629	-.86	.583	.401	3.94
27	3	401	31.700	31.816	-.46	.185	1.300	1.324	-.35	.908	.649	5.61
28	4	803	27.100	29.322	-8.89	.110	.770	.905	-1.97	1.220	.916	6.59
29	5	3900	3.830	12.179	-33.40	-.000	0.000	.000	-.00	.026	.644	-13.38
30	6	19560	0.000	.694	-2.77	-.000	0.000	-.000	.00	0.000	.100	-2.17

TEST NO 6 INITIAL CONDITIONS:
PH = 2.78   FECL3, MMOLAR = 2.8
T, C = 25.0   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
31	1	0	3.430			.290	1.720			.302		
32	2	3582	1.640	2.198	-2.23	.199	1.100	1.279	-2.61	.831	.671	3.48
33	3	8958	.660	1.162	-2.01	.133	.670	.941	-3.96	.798	.889	-1.98
34	4	17922	0.000	.441	-1.76	.092	.840	.717	1.81	.981	.998	-.36
35	5	87215	0.000	.003	-.01	.067	.900	.572	4.80	1.027	1.048	-.45
36	6	436080	0.000	.000	-.00	.067	.820	.571	3.65	1.023	1.048	-.55

TEST NO 7 INITIAL CONDITIONS:
PH = 2.77   FECL3, MMOLAR = .2
T, C = 24.9   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
37	1	0	34.300			.290	1.660			0.000		
38	2	162	32.500	34.206	-6.82	.283	.854	1.627	-11.47	.029	.037	-.20
39	3	401	32.500	34.066	-6.26	.273	.595	1.579	-14.60	.076	.090	-.30
40	4	803	32.500	33.832	-5.33	.256	.374	1.501	-16.72	.119	.171	-1.14
41	5	3900	31.300	32.077	-3.11	.149	-9.990	.982	0.00	.652	.608	.96
42	6	19487	21.100	23.302	-8.81	.000	.118	-.003	1.79	.973	.586	8.53

TEST NO 8 INITIAL CONDITIONS:
PH = 2.74   FECL3, MMOLAR = .4
T, C = 25.1   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
43	1	0	3.430			.290	2.030			0.000		
44	2	3582	3.440	3.190	1.00	.266	1.940	1.901	.57	.139	.139	.01
45	3	8958	3.290	2.860	1.72	.234	1.790	1.731	.86	.323	.304	.41
46	4	17922	2.780	2.389	1.57	.192	1.610	1.499	1.62	.596	.506	1.94
47	5	87215	.760	.677	.33	.069	.823	.750	1.07	1.210	.980	4.99
48	6	444420	0.000	.005	-.02	.033	-9.990	.483	0.00	-9.990	1.063	0.00

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| | | | HYDROGEN PEROXIDE | | | METHANOL | FORMALDEHYDE | | | FORMIC ACID | | |
| | | | CONCENTRATION [MILLIMOLAR] | | WEIGHTED RESIDUAL | CONCENTRATION [MILLIMOLAR] | CONCENTRATION [MILLIMOLAR] | | WEIGHTED RESIDUAL | CONCENTRATION [MILLIMOLAR] | | WEIGHTED RESIDUAL |
CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
TEST NO 9	INITIAL CONDITIONS:											
	PH = 2.74 FECL3, MMOLAR = 1.1											
	T. C = 35.2 NACL, MMOLAR = 0.0											
	NA2SO4, MMOLAR = 0.0											
49	1	0	10.300			2.950	19.800			0.000		
50	2	150	8.830	9.889	-4.23	2.894	22.300	19.514	4.19	.554	.328	.50
51	3	365	8.680	9.312	-2.53	2.819	19.900	19.126	1.16	1.430	.754	1.51
52	4	731	8.050	8.396	-1.39	2.703	-9.990	18.527	0.00	-9.990	1.384	0.00
53	5	3570	4.080	3.596	1.94	2.144	14.600	15.577	-1.47	5.030	4.160	1.94
54	6	17832	.259	.057	.81	1.771	8.980	13.539	-6.85	5.410	5.817	-.91
TEST NO 10	INITIAL CONDITIONS:											
	PH = 2.86 FECL3, MMOLAR = .9											
	T. C = 35.0 NACL, MMOLAR = 0.0											
	NA2SO4, MMOLAR = 0.0											
55	1	0	10.300			0.000	0.000			0.000		
56	2	1463	8.980	8.074	3.62	0.000	0.000	-.000	-.00	0.000	-.000	-.00
57	3	3665	7.630	5.929	6.80	0.000	0.000	-.000	-.00	0.000	-.000	-.00
58	4	7331	6.010	3.737	9.09	0.000	0.000	-.000	-.00	0.000	-.000	-.00
59	5	35670	1.560	.570	3.96	0.000	0.000	-.000	-.00	0.000	-.000	-.00
60	6	178338	0.000	.048	-.19	0.000	0.000	-.000	-.00	0.000	-.000	-.00
TEST NO 11	INITIAL CONDITIONS:											
	PH = 2.75 FECL3, MMOLAR = 1.1											
	T. C = 15.5 NACL, MMOLAR = 0.0											
	NA2SO4, MMOLAR = 0.0											
61	1	0	10.300			2.950	19.500			0.000		
62	2	936	9.080	9.835	-3.02	2.887	18.030	19.179	-1.63	0.000	.367	-.78
63	3	2370	8.840	9.159	-1.28	2.798	19.150	18.728	.60	.492	.860	-.78
64	4	4661	8.530	8.168	1.45	2.673	18.580	18.085	.70	1.100	1.529	-.91
65	5	22800	5.740	3.230	10.04	2.099	15.050	15.080	-.04	3.960	4.323	-.77
66	6	103680	.522	.033	1.96	1.761	15.190	13.250	2.76	9.574	5.799	7.97
TEST NO 12	INITIAL CONDITIONS:											
	PH = 2.75 FECL3, MMOLAR = 1.1											
	T. C = 15.4 NACL, MMOLAR = 0.0											
	NA2SO4, MMOLAR = 0.0											
67	1	0	10.300			0.000	0.000			0.000		
68	2	9323	3.140	5.716	-10.30	0.000	0.000	0.000	0.00	0.000	0.000	0.00
69	3	24720	1.400	2.827	-5.71	0.000	0.000	0.000	0.00	0.000	0.000	0.00
70	4	46625	.660	1.400	-2.96	0.000	0.000	0.000	0.00	0.000	0.000	0.00
71	5	226920	0.000	.040	-.16	0.000	0.000	0.000	0.00	0.000	0.000	0.00

			HYDROGEN PEROXIDE			METHANOL	FORMALDEHYDE			FORMIC ACID		
			CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL
CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC

TEST NO 13 INITIAL CONDITIONS:
  PH   = 2.99   FECL3, MMOLAR = 3.2
  T, C = 25.7   NACL, MMOLAR = 0.0
  NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
72	1	0	10.300			.290	1.760			.218		
73	2	468	9.350	9.624	-1.10	.244	1.480	1.538	-.85	.482	.424	1.26
74	3	1176	8.410	8.662	-1.01	.187	1.260	1.252	.11	.686	.653	.73
75	4	2352	7.370	7.242	.51	.118	1.000	.889	1.63	.844	.884	-.88
76	5	11640	3.210	1.467	6.97	.001	.455	.066	5.69	1.010	.940	1.53
77	6	57660	.260	.044	.86	-.000	.207	.000	3.02	.792	.682	2.38

TEST NO 14 INITIAL CONDITIONS:
  PH   = 3.00   FECL3, MMOLAR = .3
  T, C = 24.8   NACL, MMOLAR = 0.0
  NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
78	1	0	10.300			.290	2.200			0.000		
79	2	468	10.100	10.239	-.56	.284	2.190	2.165	.36	.078	.039	.83
80	3	1176	9.860	10.146	-1.15	.274	2.120	2.113	.10	.176	.094	1.74
81	4	2352	9.770	9.992	-.89	.259	2.020	2.028	-.12	.359	.181	3.80
82	5	11580	7.560	8.792	-4.93	.158	1.160	1.437	-3.97	1.180	.690	10.45
83	6	74880	.425	4.149	-14.89	-.000	.065	.029	.52	0.000	.964	-20.56

TEST NO 15 INITIAL CONDITIONS:
  PH   = 2.50   FECL3, MMOLAR = 3.1
  T, C = 25.4   NACL, MMOLAR = 0.0
  NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
84	1	0	10.300			.290	1.830			.299		
85	2	468	9.230	9.285	-.22	.241	1.310	1.584	-4.11	.527	.518	.20
86	3	1176	8.120	7.928	.77	.183	1.360	1.285	1.13	.839	.748	2.04
87	4	2352	6.320	6.094	.90	.118	1.030	.933	1.45	1.120	.963	3.50
88	5	11460	.800	1.058	-1.03	.007	.328	.172	2.34	1.220	1.094	2.82
89	6	57197	0.000	.023	-.09	-.000	.263	.045	3.27	1.050	.972	1.74

TEST NO 16 INITIAL CONDITIONS:
  PH   = 2.51   FECL3, MMOLAR = .2
  T, C = 24.5   NACL, MMOLAR = 0.0
  NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
90	1	0	10.300			.290	1.930			0.000		
91	2	468	9.950	10.239	-1.16	.285	1.850	1.903	-.77	.041	.031	.21
92	3	1176	9.760	10.147	-1.55	.277	1.500	1.862	-5.26	.109	.075	.74
93	4	2352	9.730	9.993	-1.05	.264	1.360	1.796	-6.34	.741	.143	12.91
94	5	11441	8.840	8.863	-.09	.180	1.360	1.350	.14	.730	.544	4.02
95	6	62220	2.790	4.683	-7.57	.009	.148	.219	-1.03	1.210	1.016	4.20

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			HYDROGEN PEROXIDE			METHANOL	FORMALDEHYDE			FORMIC ACID		
			CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL
CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC

TEST NO 17   INITIAL CONDITIONS:
                PH   = 2.75   FECL3, MMOLAR = 1.1
                T, C = 25.1   NACL, MMOLAR = 0.0
                              NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
96	1	0	34.300			2.950	20.180			0.000		
97	2	360	25.800	32.875	-28.30	2.764	19.790	19.214	.85	.750	1.063	-.69
98	3	893	24.800	30.823	-24.09	2.515	18.500	17.902	.89	1.930	2.383	-1.00
99	4	1793	23.800	27.638	-15.35	2.155	17.380	15.965	2.09	3.590	4.152	-1.24
100	5	8723	15.800	12.218	14.33	.740	11.340	7.609	5.52	10.820	9.689	2.49
101	6	40860	2.290	.714	6.30	.089	3.860	2.381	2.19	15.550	10.593	10.90

TEST NO 18   INITIAL CONDITIONS:
                PH   = 2.76   FECL3, MMOLAR = 1.0
                T, C = 25.0   NACL, MMOLAR = 0.0
                              NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
102	1	0	34.300			0.000	0.000			0.000		
103	2	3582	14.700	13.917	3.13	0.000	0.000	0.000	0.00	0.000	0.000	0.00
104	3	8958	4.690	5.678	-3.95	0.000	0.000	0.000	0.00	0.000	0.000	0.00
105	4	18480	1.220	2.154	-3.73	0.000	0.000	0.000	0.00	0.000	0.000	0.00
106	5	87215	0.000	.133	-.53	0.000	0.000	-.000	-.00	0.000	-.000	-.00

TEST NO 19   INITIAL CONDITIONS:
                PH   = 2.76   FECL3, MMOLAR = 1.2
                T, C = 24.6   NACL, MMOLAR = 0.0
                              NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
107	1	0	3.430			2.950	20.000			0.000		
108	2	360	3.200	3.293	-.37	2.931	-9.990	19.903	0.00	-9.990	.113	0.00
109	3	893	2.930	3.096	-.66	2.905	20.781	19.767	1.54	.193	.268	-.17
110	4	1793	2.780	2.791	-.04	2.864	21.075	19.559	2.31	.415	.500	-.19
111	5	8723	1.530	1.201	1.31	2.664	18.245	18.515	-.41	1.606	1.600	.01
112	6	43980	0.000	.017	-.07	2.521	18.510	17.767	1.13	2.776	2.340	.99

TEST NO 20   INITIAL CONDITIONS:
                PH   = 2.74   FECL3, MMOLAR = .9
                T, C = 25.5   NACL, MMOLAR = 0.0
                              NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
113	1	0	3.430			0.000	0.000			0.000		
114	2	3582	2.740	2.621	.48	0.000	0.000	-.000	-.00	0.000	-.000	-.00
115	3	8958	1.840	1.913	-.29	0.000	0.000	-.000	-.00	0.000	-.000	-.00
116	4	17922	1.130	1.257	-.51	0.000	0.000	-.000	-.00	0.000	-.000	-.00
117	5	87215	.140	.206	-.26	-.000	0.000	-.000	-.00	0.000	-.000	-.00
118	6	437700	0.000	.007	-.03	-.000	0.000	-.000	-.00	0.000	-.000	-.00

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| | | | HYDROGEN PEROXIDE | | | METHANOL | FORMALDEHYDE | | | FORMIC ACID | | |
| | | | CONCENTRATION [MILLIMOLAR] | | WEIGHTED RESIDUAL | CONCENTRATION [MILLIMOLAR] | CONCENTRATION [MILLIMOLAR] | | WEIGHTED RESIDUAL | CONCENTRATION [MILLIMOLAR] | | WEIGHTED RESIDUAL |
CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
TEST NO 21												
			PH = 2.73 FECL3, MMOLAR = .9									
			T, C = 25.2 NACL, MMOLAR = 0.0									
			NA2SO4, MMOLAR = 0.0									
119	1	0	10.300			.290	1.980			.074		
120	2	468	9.970	10.068	-.39	.272	1.910	1.885	.37	.025	.173	-3.22
121	3	1176	9.700	9.721	-.08	.246	1.790	1.748	.61	.428	.305	2.67
122	4	2352	9.100	9.166	-.27	.207	1.550	1.542	.12	.692	.487	4.47
123	5	11441	3.890	5.598	-6.83	.043	.283	.534	-3.67	1.230	1.065	3.59
124	6	62700	0.000	.656	-2.62	-.001	.032	-.001	.48	.412	.621	-4.55
TEST NO 22												
			PH = 2.75 FECL3, MMOLAR = 1.1									
			T, C = 25.1 NACL, MMOLAR = 0.0									
			NA2SO4, MMOLAR = 0.0									
125	1	0	10.300			.290	1.770			.057		
126	2	468	9.850	9.984	-.54	.267	1.690	1.661	.41	.191	.172	.41
127	3	1176	9.290	9.525	-.94	.237	1.580	1.509	1.01	.391	.317	1.56
128	4	2352	8.600	8.802	-.81	.192	1.340	1.286	.77	.665	.508	3.33
129	5	12480	2.690	4.453	-7.05	.025	.180	.315	-1.93	.833	.978	-3.07
130	6	66600	0.000	.339	-1.36	-.001	.070	.000	1.00	.285	.541	-5.42
TEST NO 23												
			PH = 2.75 FECL3, MMOLAR = 1.1									
			T, C = 24.8 NACL, MMOLAR = 0.0									
			NA2SO4, MMOLAR = 0.0									
131	1	0	10.300			.290	2.130			.056		
132	2	468	10.200	10.033	.67	.269	2.030	2.016	.21	.232	.176	1.22
133	3	1176	9.550	9.637	-.35	.240	1.860	1.854	.09	.440	.331	2.36
134	4	2352	9.090	9.006	.34	.197	1.640	1.611	.42	.749	.541	4.51
135	5	11760	3.230	5.321	-8.36	.031	.250	.502	-3.68	.947	1.142	-4.22
136	6	75000	0.000	.366	-1.46	-.000	.060	-.000	.88	.199	.596	-8.59
TEST NO 24												
			PH = 2.74 FECL3, MMOLAR = 3.4									
			T, C = 34.7 NACL, MMOLAR = 0.0									
			NA2SO4, MMOLAR = 0.0									
137	1	0	10.300			.290	1.770			.346		
138	2	192	9.630	9.593	.15	.244	-9.990	1.546	0.00	.376	.542	-3.59
139	3	480	8.610	8.611	-.00	.188	1.160	1.263	-1.49	.879	.757	2.63
140	4	960	7.350	7.163	.75	.119	.847	.901	-.78	1.040	.976	1.39
141	5	4680	2.470	1.643	3.31	.001	.237	.076	2.35	.910	1.016	-2.29
142	6	23700	0.000	.042	-.17	-.000	-9.990	.000	0.00	.903	.733	3.68

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			HYDROGEN PEROXIDE			METHANOL	FORMALDEHYDE			FORMIC ACID		
			CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL
CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC

TEST NO 25   INITIAL CONDITIONS:
PH   = 2.76   FECL3, MMOLAR = .3
T, C = 34.4   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

143	1	0	10.300			.290	1.950			0.000		
144	2	192	10.400	10.240	.64	.284	1.900	1.919	-.27	.039	.035	.09
145	3	480	10.200	10.151	.20	.275	1.870	1.873	-.04	.094	.085	.19
146	4	960	10.100	10.001	.40	.261	1.850	1.798	.76	.188	.163	.54
147	5	4800	8.550	8.840	-1.16	.163	1.220	1.274	-.78	.793	.619	3.77
148	6	24660	2.180	5.007	-11.31	.001	.075	.107	-.46	.739	.973	-5.06

TEST NO 26   INITIAL CONDITIONS:
PH   = 2.75   FECL3, MMOLAR = 3.1
T, C = 15.9   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

149	1	0	10.300			.290	1.820			.155		
150	2	1223	9.380	9.222	.63	.233	1.580	1.539	.60	.458	.420	.82
151	3	3060	8.200	7.825	1.50	.169	1.250	1.208	.61	.775	.681	2.03
152	4	6114	6.630	5.962	2.67	.101	.814	.830	-.23	1.020	.910	2.37
153	5	29766	.981	.915	.26	.004	.108	.129	-.30	.491	.995	-10.83
154	6	153480	0.000	.010	-.04	.000	.078	.034	.63	.331	.884	-11.90

TEST NO 27   INITIAL CONDITIONS:
PH   = 2.58   FECL3, MMOLAR = .3
T, C = 14.9   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

155	1	0	10.300			.290	1.890			0.000		
156	2	1223	10.530	10.183	1.39	.281	1.900	1.845	.80	.052	.051	.03
157	3	3060	10.150	10.007	.57	.268	1.790	1.779	.16	.114	.120	-.14
158	4	6114	9.920	9.718	.81	.247	1.850	1.673	2.57	.188	.227	-.83
159	5	29766	9.090	7.640	5.80	.126	1.340	1.016	4.70	.735	.749	-.31
160	6	151380	2.430	2.270	.64	.000	.140	.050	1.31	1.208	.884	6.98

TEST NO 28   INITIAL CONDITIONS:
PH   = 3.02   FECL3, MMOLAR = 1.1
T, C = 25.0   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

161	1	0	34.300			.290	1.780			.043		
162	2	162	32.300	33.982	-6.73	.269	1.690	1.678	.18	.171	.151	.43
163	3	401	31.700	33.510	-7.24	.240	1.580	1.534	.68	.309	.291	.39
164	4	803	31.000	32.715	-6.86	.195	1.390	1.310	1.17	.515	.485	.66
165	5	3900	26.800	26.434	1.47	.014	.312	.231	1.20	1.110	.968	3.12
166	6	19487	12.600	4.991	30.44	-.000	.019	-.000	.28	.142	.029	2.48

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			HYDROGEN PEROXIDE			METHANOL	FORMALDEHYDE			FORMIC ACID		
			CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL
CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC

TEST NO 29   INITIAL CONDITIONS:
        PH = 2.97   FECL3, MMOLAR = .9
        T, C = 25.4   NACL, MMOLAR = 0.0
                     NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
167	1	0	3.430			.290	1.510			.078		
168	2	3582	2.960	3.020	-.24	.250	1.390	1.334	.82	.318	.256	1.35
169	3	8958	2.240	2.493	-1.01	.203	1.250	1.123	1.86	.516	.441	1.62
170	4	17922	1.540	1.837	-1.19	.149	1.080	.876	2.98	.680	.623	1.24
171	5	87215	.260	.251	.04	.045	.810	.349	6.73	1.120	.854	5.77
172	6	436980	0.000	-.000	.00	.030	.772	.266	7.39	1.120	.859	5.65

TEST NO 30   INITIAL CONDITIONS:
        PH = 2.54   FECL3, MMOLAR = 1.0
        T, C = 24.6   NACL, MMOLAR = 0.0
                     NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
173	1	0	34.300			.290	2.000			.073		
174	2	162	32.700	33.796	-4.38	.266	1.970	1.874	1.40	.215	.202	.28
175	3	401	32.400	33.052	-2.61	.233	1.650	1.699	-.72	.311	.367	-1.22
176	4	803	31.500	31.804	-1.22	.184	1.710	1.431	4.07	.543	.590	-1.03
177	5	3900	25.100	22.382	10.87	.009	.560	.240	4.67	1.540	1.085	9.87
178	6	19680	1.470	2.682	-4.85	-.000	0.000	-.005	.08	.084	.187	-2.24

TEST NO 31   INITIAL CONDITIONS:
        PH = 2.50   FECL3, MMOLAR = 1.0
        T, C = 25.1   NACL, MMOLAR = 0.0
                     NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
179	1	0	3.430			.290	1.750			.114		
180	2	3582	2.710	2.779	-.27	.241	1.670	1.512	2.28	.403	.346	1.23
181	3	8958	-9.990	2.052	0.00	.191	-9.990	1.262	0.00	-9.990	.555	0.00
182	4	17940	1.090	1.264	-.70	.139	1.180	.996	2.65	.953	.742	4.51
183	5	87215	0.000	.090	-.36	.070	.933	.607	4.69	1.110	.938	3.68
184	6	436080	0.000	-.000	.00	.064	.853	.571	4.05	1.070	.950	2.56

TEST NO 32 - INITIAL CONDITIONS:
        PH = 2.73   FECL3, MMOLAR = 3.2
        T, C = 24.6   NACL, MMOLAR = 0.0
                     NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
185	1	0	10.300			2.950	19.800			0.000		
186	2	360	8.650	9.334	-2.74	2.822	18.480	19.141	-1.02	.930	.738	.44
187	3	893	7.820	8.027	-.83	2.657	19.000	18.290	1.10	1.890	1.627	.60
188	4	1793	7.030	6.195	3.34	2.438	16.660	17.141	-.74	2.910	2.749	.37
189	5	8723	2.290	.791	6.00	1.846	13.020	13.956	-1.44	5.930	5.491	1.01
190	6	43607	0.000	-.000	.00	1.765	13.640	13.508	.20	7.710	5.838	4.29

			HYDROGEN PEROXIDE			METHANOL	FORMALDEHYDE			FORMIC ACID		
			CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL
CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC

TEST NO 33   INITIAL CONDITIONS:
          PH   = 2.76   FECL3, MMOLAR = 3.1
          T, C = 25.0   NACL, MMOLAR = 0.0
                        NA2SO4, MMOLAR = 0.0

191	1	0	10.300			0.000	0.000			0.000		
192	2	3582	1.780	1.881	-.41	0.000	0.000	0.000	0.00	0.000	0.000	0.00
193	3	8958	.520	.507	.05	0.000	0.000	-.000	-.00	0.000	-.000	-.00
194	4	18060	.270	.121	.59	0.000	0.000	-.000	-.00	0.000	-.000	-.00
195	5	87215	0.000	.006	-.02	0.000	0.000	-.000	-.00	0.000	-.000	-.00

TEST NO 34   INITIAL CONDITIONS:
          PH   = 2.75   FECL3, MMOLAR = .3
          T, C = 24.8   NACL, MMOLAR = 0.0
                        NA2SO4, MMOLAR = 0.0

196	1	0	10.300			2.950	22.500			0.000		
197	2	360	9.000	10.136	-4.54	2.929	21.700	22.382	-.99	0.000	.136	-.29
198	3	893	8.690	9.894	-4.81	2.898	20.500	22.211	-2.49	0.000	.328	-.71
199	4	1793	8.900	9.496	-2.39	2.849	-9.990	21.936	0.00	-9.990	.629	0.00
200	5	8723	7.920	6.833	4.35	2.536	21.100	20.174	1.34	0.000	2.428	-5.24
201	6	43800	2.490	1.224	5.06	1.944	15.200	16.727	-2.22	7.920	5.488	5.25

TEST NO 35   INITIAL CONDITIONS:
          PH   = 2.75   FECL3, MMOLAR = .2
          T, C = 25.1   NACL, MMOLAR = 0.0
                        NA2SO4, MMOLAR = 0.0

202	1	0	10.300			0.000	0.000			0.000		
203	2	3582	9.660	9.526	.53	0.000	0.000	0.000	0.00	0.000	0.000	0.00
204	3	8958	8.140	8.526	-1.54	0.000	0.000	0.000	0.00	0.000	0.000	0.00
205	4	17640	5.660	7.226	-6.27	0.000	0.000	0.000	0.00	0.000	0.000	0.00
206	5	87215	.760	2.679	-7.68	0.000	0.000	0.000	0.00	0.000	0.000	0.00
207	6	169560	0.000	1.248	-4.99	0.000	0.000	0.000	0.00	0.000	0.000	0.00

TEST NO 36   INITIAL CONDITIONS:
          PH   = 3.00   FECL3, MMOLAR = 1.1
          T, C = 24.9   NACL, MMOLAR = 0.0
                        NA2SO4, MMOLAR = 0.0

208	1	0	10.300			2.950	20.100			0.000		
209	2	360	8.890	9.948	-4.23	2.903	-9.990	19.855	0.00	-9.990	.280	0.00
210	3	893	8.180	9.436	-5.02	2.836	19.600	19.508	.15	-9.990	.664	0.00
211	4	1793	7.950	8.608	-2.63	2.731	18.200	18.961	-1.22	-9.990	1.243	0.00
212	5	8723	4.330	3.960	1.48	2.189	-9.990	16.083	0.00	-9.990	3.977	0.00
213	6	43607	.275	.060	.86	1.778	11.700	13.818	-3.41	-9.990	5.839	0.00

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			HYDROGEN PEROXIDE			METHANOL	FORMALDEHYDE			FORMIC ACID		
			CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL
CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC

TEST NO 37   INITIAL CONDITIONS:
PH = 3.00   FECL3, MMOLAR = 1.0
T, C = 25.1   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
214	1	0	10.300			0.000	0.000			0.000		
215	2	3582	7.370	7.497	-.51	0.000	0.000	0.000	0.00	.000	-.000	-.00
216	3	8958	4.960	4.994	-.14	0.000	0.000	-.000	-.00	0.000	-.000	-.00
217	4	17922	2.850	2.896	-.18	0.000	0.000	-.000	-.00	0.000	-.000	-.00
218	5	87215	.250	.277	-.11	0.000	0.000	-.000	-.00	0.000	-.000	-.00
219	6	436080	0.000	.010	-.04	-.000	0.000	-.000	-.00	0.000	-.000	-.00

TEST NO 38   INITIAL CONDITIONS:
PH = 2.50   FECL3, MMOLAR = 1.1
T, C = 25.0   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
220	1	0	10.300			2.950	19.390			0.000		
221	2	360	9.460	9.874	-1.66	2.892	19.480	19.096	.58	0.000	.336	-.75
222	3	893	8.950	9.260	-1.24	2.811	19.240	18.685	.83	.399	.787	-.86
223	4	1793	8.950	8.290	2.64	2.688	18.730	18.056	1.01	.917	1.446	-1.18
224	5	8723	5.610	3.451	8.63	2.121	17.470	15.105	3.55	4.459	4.208	.56
225	6	43980	.440	.046	1.58	1.760	15.320	13.157	3.25	9.425	5.783	8.12

TEST NO 39   INITIAL CONDITIONS:
PH = 2.50   FECL3, MMOLAR = 1.2
T, C = 25.0   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
226	1	0	10.300			0.000	0.000			0.000		
227	2	3582	5.120	4.075	4.18	0.000	0.000	-.000	-.00	0.000	-.000	-.00
228	3	8958	2.550	1.691	3.44	0.000	0.000	-.000	-.00	0.000	-.000	-.00
229	4	17922	1.400	.664	2.94	0.000	0.000	-.000	-.00	0.000	-.000	-.00
230	5	87215	0.000	.061	-.24	-.000	0.000	.000	.00	0.000	.000	.00

TEST NO 40   INITIAL CONDITIONS:
PH = 2.87   FECL3, MMOLAR = 1.0
T, C = 35.2   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
231	1	0	34.300			.290	1.890			.074		
232	2	66	32.600	34.018	-5.67	.270	1.780	1.790	-.15	.179	.177	.04
233	3	162	32.400	33.605	-4.82	.243	1.690	1.651	.57	.321	.311	.21
234	4	330	31.700	32.869	-4.68	.199	1.200	1.423	-3.28	.387	.509	-2.68
235	5	1596	26.900	27.524	-2.50	.019	.348	.314	.50	.615	1.045	-9.42
236	6	7968	6.620	7.305	-2.74	-.000	0.000	-.002	.03	.025	.029	-.08

| | | | HYDROGEN PEROXIDE | | | METHANOL | FORMALDEHYDE | | | FORMIC ACID | | |
| | | | CONCENTRATION [MILLIMOLAR] | | WEIGHTED RESIDUAL | CONCENTRATION [MILLIMOLAR] | CONCENTRATION [MILLIMOLAR] | | WEIGHTED RESIDUAL | CONCENTRATION [MILLIMOLAR] | | WEIGHTED RESIDUAL |
CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
TEST NO 41		INITIAL CONDITIONS: PH = 2.88 FECL3, MMOLAR = .8 T. C = 34.8 NACL, MMOLAR = 0.0 NA2SO4, MMOLAR = 0.0										
237	1	0	3.430			.290	1.980			.069		
238	2	1463	2.690	3.070	-1.52	.254	1.750	1.791	-.61	.339	.260	1.71
239	3	3665	2.240	2.632	-1.57	.213	1.550	1.572	-.32	.564	.458	2.30
240	4	7331	1.580	2.029	-1.79	.162	1.350	1.287	.92	.760	.681	1.72
241	5	35670	.262	.350	-.35	.048	-9.990	.576	0.00	-9.990	1.054	0.00
242	6	178338	0.000	.001	-.00	.029	.756	.430	4.77	1.120	1.083	.80
TEST NO 42		INITIAL CONDITIONS: PH = 2.75 FECL3, MMOLAR = 1.1 T. C = 15.8 NACL, MMOLAR = 0.0 NA2SO4, MMOLAR = 0.0										
243	1	0	34.300			.290	1.840			.122		
244	2	420	28.000	33.711	-22.85	.261	1.750	1.694	.81	.196	.267	-1.54
245	3	1043	27.800	32.850	-20.20	.221	1.710	1.494	3.14	.342	.448	-2.28
246	4	2082	27.500	31.470	-15.88	.166	1.500	1.202	4.33	.532	.675	-3.09
247	5	10140	22.700	21.368	5.33	.001	-9.990	.096	0.00	.032	.967	-20.20
248	6	48960	1.090	2.648	-6.23	-.000	.025	-.001	.38	0.000	.088	-1.89
TEST NO 43		INITIAL CONDITIONS: PH = 2.75 FECL3, MMOLAR = 1.2 T. C = 15.5 NACL, MMOLAR = 0.0 NA2SO4, MMOLAR = 0.0										
249	1	0	3.430			.290	1.930			.127		
250	2	9323	3.210	2.732	1.91	.231	1.670	1.627	.63	.455	.415	.87
251	3	24240	2.130	1.892	.95	.169	1.410	1.289	1.77	.725	.684	.90
252	4	46625	1.580	1.130	1.80	.118	1.140	.999	2.06	.962	.871	1.98
253	5	226920	0.000	.016	-.06	.055	.731	.601	1.91	1.100	1.048	1.12
TEST NO 44		INITIAL CONDITIONS: PH = 2.75 FECL3, MMOLAR = 1.5 T. C = 25.2 NACL, MMOLAR = 0.0 NA2SO4, MMOLAR = 0.0										
254	1	0	10.300			.290	1.930			.082		
255	2	468	10.000	9.921	.32	.263	1.790	1.790	-.01	.228	.225	.07
256	3	1176	9.240	9.370	-.52	.226	1.610	1.598	.17	.440	.402	.81
257	4	2352	8.470	8.520	-.20	.175	1.330	1.323	.10	.730	.625	2.26
258	5	11520	2.580	4.068	-5.95	.016	.120	.292	-2.49	.710	1.065	-7.61
259	6	66600	0.000	.204	-.82	-.000	.020	-.000	.30	.179	.604	-9.12

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| | | | HYDROGEN PEROXIDE | | | METHANOL | FORMALDEHYDE | | | FORMIC ACID | | |
| | | | CONCENTRATION [MILLIMOLAR] | | WEIGHTED RESIDUAL | CONCENTRATION [MILLIMOLAR] | CONCENTRATION [MILLIMOLAR] | | WEIGHTED RESIDUAL | CONCENTRATION [MILLIMOLAR] | | WEIGHTED RESIDUAL |
CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
TEST NO 45	INITIAL CONDITIONS:											
	PH = 2.78 FECL3, MMOLAR = 1.0											
	T, C = 25.2 NACL, MMOLAR = 0.0											
	NA2SO4, MMOLAR = 0.0											
260	1	0	10.300			.290	1.850			.119		
261	2	468	9.810	10.035	-.90	.269	-9.990	1.748	0.00	.246	.222	.51
262	3	1176	9.420	9.645	-.90	.241	1.510	1.603	-1.37	.496	.358	3.00
263	4	2352	8.510	9.011	-2.00	.198	1.190	1.384	-2.84	.755	.543	4.60
264	5	12240	2.100	4.919	-11.28	.028	.096	.368	-3.98	.780	1.046	-5.79
265	6	57960	0.000	.567	-2.27	-.000	.011	-.001	.16	.240	.579	-7.37
TEST NO 46	INITIAL CONDITIONS:											
	PH = 2.76 FECL3, MMOLAR = 1.1											
	T, C = 24.9 NACL, MMOLAR = 0.0											
	NA2SO4, MMOLAR = 0.0											
266	1	0	10.300			.290	1.970			.093		
267	2	468	9.740	10.016	-1.10	.268	1.880	1.858	.32	.244	.208	.77
268	3	1176	9.450	9.598	-.59	.238	1.680	1.700	-.29	.419	.357	1.33
269	4	2352	8.700	8.935	-.94	.195	1.450	1.464	-.21	.690	.557	2.86
270	5	11441	3.610	5.032	-5.69	.030	.270	.434	-2.37	1.084	1.088	-.09
271	6	62400	.260	.481	-.88	-.000	.040	-.000	.58	.357	.613	-5.47
TEST NO 47	INITIAL CONDITIONS:											
	PH = 3.27 FECL3, MMOLAR = 1.2											
	T, C = 25.0 NACL, MMOLAR = 0.0											
	NA2SO4, MMOLAR = 0.0											
272	1	0	10.300			.290	1.740			.058		
273	2	468	10.600	10.113	1.95	.273	1.690	1.659	.45	.107	.145	-.81
274	3	1176	10.500	9.858	2.57	.250	1.660	1.549	1.61	.163	.253	-1.94
275	4	2352	10.200	9.454	2.99	.216	1.580	1.382	2.87	.224	.404	-3.88
276	5	11760	9.700	6.704	11.98	.052	1.330	.493	12.15	.545	.936	-8.44
277	6	56820	7.650	1.214	25.74	-.000	.689	-.000	10.01	1.040	.367	14.50
TEST NO 48	INITIAL CONDITIONS:											
	PH = 2.25 FECL3, MMOLAR = 1.1											
	T, C = 25.5 NACL, MMOLAR = 0.0											
	NA2SO4, MMOLAR = 0.0											
278	1	0	10.300			.290	2.290			.053		
279	2	468	10.500	10.151	1.40	.280	1.900	2.232	-4.82	.142	.115	.59
280	3	1176	10.000	9.944	.23	.266	1.800	2.152	-5.12	.250	.196	1.17
281	4	2352	9.600	9.609	-.04	.244	1.680	2.027	-5.05	.406	.315	1.95
282	5	12420	5.840	6.307	-1.87	.087	.807	1.027	-3.20	1.020	1.041	-.46
283	6	62400	.380	1.234	-3.41	-.000	.300	.100	2.91	1.290	1.130	3.46

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| | | | HYDROGEN PEROXIDE | | | METHANOL | FORMALDEHYDE | | | FORMIC ACID | | |
| | | | CONCENTRATION [MILLIMOLAR] | | WEIGHTED RESIDUAL | CONCENTRATION [MILLIMOLAR] | CONCENTRATION [MILLIMOLAR] | | WEIGHTED RESIDUAL | CONCENTRATION [MILLIMOLAR] | | WEIGHTED RESIDUAL |
CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
TEST NO 49		INITIAL CONDITIONS:										
		PH = 2.74 FECL3, MMOLAR = 1.1										
		T, C = 25.2 NACL, MMOLAR = 0.0										
		NA2SO4, MMOLAR = .5										
284	1	0	10.300			.290	2.200			.067		
285	2	468	10.100	10.013	.35	.267	2.174	2.075	1.44	.196	.196	.00
286	3	1176	9.910	9.590	1.28	.236	2.020	1.899	1.76	.342	.363	-.45
287	4	2352	9.710	8.920	3.16	.191	1.850	1.636	3.09	.569	.586	-.37
288	5	11460	6.320	5.114	4.82	.026	.823	.488	4.85	1.290	1.188	2.20
289	6	69240	0.000	.509	-2.04	-.000	.052	-.003	.80	.227	.579	-7.57
TEST NO 50		INITIAL CONDITIONS:										
		PH = 2.71 FECL3, MMOLAR = 1.2										
		T, C = 25.4 NACL, MMOLAR = 0.0										
		NA2SO4, MMOLAR = 10.0										
290	1	0	10.300			.290	1.910			.176		
291	2	468	10.500	9.991	2.04	.267	1.870	1.794	1.11	.226	.289	-1.37
292	3	1176	10.400	9.539	3.44	.236	1.800	1.632	2.45	.324	.436	-2.43
293	4	2352	10.200	8.812	5.55	.191	1.570	1.392	2.60	.463	.631	-3.64
294	5	11940	8.060	4.976	12.34	.026	1.010	.377	9.25	1.070	1.107	-.81
295	6	65400	.680	.472	.83	-.000	.015	-.001	.24	.207	.552	-7.48
TEST NO 51		INITIAL CONDITIONS:										
		PH = 2.74 FECL3, MMOLAR = 1.2										
		T, C = 25.0 NACL, MMOLAR = 0.0										
		NA2SO4, MMOLAR =200.0										
296	1	0	10.300			.290	1.820			.826		
297	2	468	10.100	10.217	-.47	.283	1.690	1.786	-1.45	.777	.852	-1.67
298	3	1176	10.100	10.092	.03	.273	1.710	1.736	-.39	.835	.889	-1.21
299	4	2352	10.100	9.891	.84	.257	1.670	1.657	.20	.875	.947	-1.60
300	5	11520	9.270	8.579	2.76	.161	1.230	1.164	.99	1.250	1.251	-.03
301	6	57540	3.790	4.263	-1.89	.003	.189	.127	.94	1.210	1.341	-2.93
TEST NO 52		INITIAL CONDITIONS:										
		PH = 2.78 FECL3, MMOLAR = 1.0										
		T, C = 25.2 NACL, MMOLAR = 6.0										
		NA2SO4, MMOLAR = 0.0										
302	1	0	10.300			.290	1.850			.114		
303	2	468	9.810	9.795	.06	.252	1.540	1.658	-1.72	.245	.303	-1.26
304	3	1176	9.280	9.073	.83	.202	1.530	1.404	1.84	.501	.524	-.49
305	4	2352	8.470	7.965	2.02	.138	1.220	1.056	2.39	.761	.774	-.28
306	5	12720	1.680	2.494	-3.25	.000	.161	.053	1.58	.807	.917	-2.38
307	6	58080	0.000	.121	-.48	-.000	.054	-.001	.81	.419	.464	-.97

			HYDROGEN PEROXIDE			METHANOL	FORMALDEHYDE			FORMIC ACID		
			CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL
CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC

TEST NO 101   INITIAL CONDITIONS:
PH   = 3.01   FECL3, MMOLAR = 1.1
T, C = 25.2   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
308	1	0	10.300			3.330	.059			.103		
309	2	468	10.200	10.164	.14	3.257	.129	.108	.30	.139	.112	.59
310	3	1176	10.200	9.951	1.00	3.151	.227	.170	.84	.200	.134	1.43
311	4	2352	9.970	9.584	1.54	2.982	.350	.247	1.50	.281	.182	2.13
312	5	11580	7.590	6.601	3.96	1.929	.840	.427	6.02	.713	.576	2.96
313	6	69660	.676	.576	.40	.567	.307	.205	1.49	1.020	.814	4.46

TEST NO 102   INITIAL CONDITIONS:
PH   = 2.51   FECL3, MMOLAR = 1.0
T, C = 25.4   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
314	1	0	10.300			3.330	.047			.092		
315	2	468	10.600	10.117	1.93	3.249	.068	.104	-.52	.113	.102	.24
316	3	1176	10.300	9.831	1.88	3.130	.102	.172	-1.02	.123	.127	-.09
317	4	2352	10.200	9.349	3.40	2.945	.171	.255	-1.23	.175	.183	-.17
318	5	12060	8.620	5.843	11.11	1.875	.558	.424	1.95	.436	.586	-3.25
319	6	62400	1.350	.593	3.03	.769	.499	.262	3.45	1.470	.827	13.88

TEST NO 103   INITIAL CONDITIONS:
PH   = 2.76   FECL3, MMOLAR = 1.1
T, C = 34.5   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
320	1	0	10.300			3.330	0.000			.082		
321	2	192	11.000	10.173	3.31	3.259	.047	.058	-.16	.097	.082	.33
322	3	480	10.600	9.968	2.53	3.155	.099	.127	-.41	.127	.099	.62
323	4	960	10.400	9.606	3.18	2.988	.186	.213	-.39	.168	.143	.55
324	5	4680	8.300	6.756	6.18	1.984	.556	.417	2.03	.505	.522	-.38
325	6	24720	2.070	.965	4.42	.651	.514	.228	4.18	1.280	.806	10.30

TEST NO 104   INITIAL CONDITIONS:
PH   = 2.75   FECL3, MMOLAR = 1.1
T, C = 15.3   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
326	1	0	10.300			3.330	.050			.107		
327	2	1223	10.500	10.106	1.58	3.239	-9.990	.112	0.00	-9.990	.117	0.00
328	3	3060	10.200	9.808	1.57	3.109	.083	.185	-1.48	.113	.145	-.70
329	4	6114	9.950	9.310	2.56	2.908	.133	.270	-2.00	.133	.206	-1.57
330	5	29766	9.120	5.886	12.94	1.826	.449	.423	.37	.365	.610	-5.29
331	6	150300	2.060	.379	6.72	.655	.415	.231	2.69	1.140	.824	6.82

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| | | | HYDROGEN PEROXIDE | | | METHANOL | FORMALDEHYDE | | | FORMIC ACID | | |
| | | | CONCENTRATION [MILLIMOLAR] | | WEIGHTED RESIDUAL | CONCENTRATION [MILLIMOLAR] | CONCENTRATION [MILLIMOLAR] | | WEIGHTED RESIDUAL | CONCENTRATION [MILLIMOLAR] | | WEIGHTED RESIDUAL |
CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
TEST NO 105												

INITIAL CONDITIONS:
PH   = 2.75   FECL3, MMOLAR = 3.2
T, C = 25.6   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
332	1	0	10.300			3.330	.021			.442		
333	2	468	9.950	9.849	.40	3.139	.169	.149	.29	.489	.424	1.40
334	3	1176	8.850	9.158	-1.23	2.878	.357	.267	1.31	.613	.453	3.48
335	4	2352	7.770	8.054	-1.14	2.509	.535	.368	2.44	.812	.538	5.95
336	5	13020	2.050	1.841	.84	1.093	.500	.336	2.40	1.184	.881	6.57
337	6	67500	0.000	.016	-.07	.767	.386	.261	1.83	1.106	.890	4.69

TEST NO 106   INITIAL CONDITIONS:
PH   = 2.75   FECL3, MMOLAR = .3
T, C = 25.0   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
338	1	0	10.300			3.330	.021			0.000		
339	2	468	10.660	10.257	1.61	3.302	.033	.044	-.16	0.000	.005	-.10
340	3	1176	10.390	10.187	.81	3.260	.038	.075	-.53	0.000	.014	-.30
341	4	2352	10.510	10.066	1.77	3.191	-9.990	.119	0.00	-9.990	.032	0.00
342	5	11460	10.070	9.027	4.17	2.704	.229	.323	-1.36	.082	.210	-2.76
343	6	62400	7.050	4.391	10.64	1.234	.713	.361	5.11	.747	.747	.00

TEST NO 107   INITIAL CONDITIONS:
PH   = 2.75   FECL3, MMOLAR = .7
T, C = 24.6   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
344	1	0	34.300			3.330	.010			.089		
345	2	162	33.600	34.157	-2.23	3.265	.036	.062	-.39	.116	.090	.56
346	3	401	33.700	33.930	-.92	3.169	.062	.125	-.94	.133	.105	.61
347	4	803	33.300	33.535	-.94	3.014	.108	.206	-1.45	.153	.144	.19
348	5	3900	32.000	30.128	7.49	1.989	.391	.419	-.41	.461	.527	-1.44
349	6	19487	13.200	12.540	2.64	.114	.042	.047	-.08	.465	.542	-1.67

TEST NO 108   INITIAL CONDITIONS:
PH   = 2.75   FECL3, MMOLAR = 1.1
T, C = 25.0   NACL, MMOLAR = 0.0
NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
350	1	0	3.430			3.330	.021			.102		
351	2	1800	3.690	3.247	1.77	3.226	.098	.097	.01	.129	.109	.43
352	3	4494	3.320	2.969	1.40	3.083	.211	.179	.46	.153	.139	.30
353	4	8988	2.700	2.529	.68	2.876	.417	.268	2.17	.227	.202	.55
354	5	44700	1.030	.503	2.11	2.088	.981	.417	8.23	.692	.499	4.17
355	6	201300	0.000	.001	-.00	1.907	.733	.421	4.55	1.100	.566	11.55

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			HYDROGEN PEROXIDE			METHANOL	FORMALDEHYDE			FORMIC ACID		
			CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL
CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
TEST NO 109	INITIAL CONDITIONS:											
PH = 2.75 FECL3, MMOLAR = 2.1												
T, C = 25.2 NACL, MMOLAR = 0.0												
NA2SO4, MMOLAR = 0.0												
356	1	0	10.300			11.100	.010			.197		
357	2	540	10.400	9.898	2.01	10.803	.052	.245	-2.80	.220	.215	.10
358	3	1350	10.200	9.251	3.80	10.387	.104	.503	-5.77	.239	.303	-1.38
359	4	2694	10.100	8.169	7.72	9.767	.120	.797	-9.79	.169	.493	-6.97
360	5	13121	8.810	2.769	24.16	7.270	.776	1.358	-8.42	.640	1.463	-17.70
361	6	65610	3.320	.012	13.23	6.191	1.820	1.392	6.20	2.380	1.874	10.87
TEST NO 110	INITIAL CONDITIONS:											
PH = 2.76 FECL3, MMOLAR = 1.1												
T, C = 25.2 NACL, MMOLAR = 0.0												
NA2SO4, MMOLAR = 0.0												
362	1	0	10.300			1.110	.015			0.000		
363	2	468	10.200	9.936	1.05	1.067	.053	.044	.13	.021	.011	.21
364	3	1176	9.850	9.410	1.76	1.005	.089	.075	.20	.042	.032	.21
365	4	2352	9.750	8.599	4.61	.914	.151	.107	.63	.083	.068	.32
366	5	11700	6.660	4.432	8.91	.494	-9.990	.133	0.00	-9.990	.230	0.00
367	6	66600	.386	.256	.52	.164	.010	.060	-.72	0.000	.260	-5.57
TEST NO 111	INITIAL CONDITIONS:											
PH = 3.24 FECL3, MMOLAR = 1.2												
T, C = 25.4 NACL, MMOLAR = 0.0												
NA2SO4, MMOLAR = 0.0												
368	1	0	10.300			3.330	0.000			.108		
369	2	468	10.500	10.190	1.24	3.264	.040	.055	-.21	.142	.106	.77
370	3	1176	9.620	10.012	-1.57	3.166	.075	.120	-.65	.153	.118	.74
371	4	2352	9.030	9.695	-2.66	3.010	.111	.203	-1.33	.139	.156	-.36
372	5	11820	5.070	7.224	-8.62	2.046	.286	.415	-1.87	.262	.508	-5.29
373	6	65220	.770	1.496	-2.91	.569	.525	.204	4.64	.353	.800	-9.61
TEST NO 112	INITIAL CONDITIONS:											
PH = 2.25 FECL3, MMOLAR = .7												
T, C = 24.5 NACL, MMOLAR = 0.0												
NA2SO4, MMOLAR = 0.0												
374	1	0	10.300			3.330	.010			.079		
375	2	468	10.100	10.249	-.60	3.305	.015	.031	-.23	.089	.078	.22
376	3	1176	10.100	10.170	-.28	3.268	.042	.060	-.26	.115	.081	.75
377	4	2352	9.990	10.065	-.30	3.220	.083	.093	-.15	.100	.087	.28
378	5	11460	9.180	9.067	.45	2.824	.322	.282	.59	.245	.200	.97
379	6	61500	3.900	5.833	-7.73	1.817	.662	.418	3.58	1.200	.586	13.37

			HYDROGEN PEROXIDE			METHANOL	FORMALDEHYDE			FORMIC ACID		
			CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL	CONCENTRATION [MILLIMOLAR]		WEIGHTED RESIDUAL
CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC

TEST NO 113   INITIAL CONDITIONS:
PH   = 2.74   FECL3, MMOLAR = 1.1
T, C = 25.1   NACL, MMOLAR = 0.0
                NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
380	1	0	10.300			3.330	.032			.067		
381	2	468	10.240	10.135	.42	3.247	.007	.092	-1.24	.084	.076	.16
382	3	1176	9.950	9.874	.30	3.125	.126	.164	-.55	.105	.104	.03
383	4	2352	9.920	9.431	1.96	2.937	.219	.250	-.45	.158	.162	-.09
384	5	12660	7.730	5.947	7.13	1.801	.687	.420	3.85	.613	.598	.33
385	6	66600	.260	.527	-1.07	.630	.258	.223	.51	.993	.811	3.90

TEST NO 114   INITIAL CONDITIONS:
PH   = 2.79   FECL3, MMOLAR = 1.1
T, C = 25.6   NACL, MMOLAR = 0.0
                NA2SO4, MMOLAR = 0.0

CASE NO	OBS NO	TIME [SEC]	OBS	CALC	(OBS-CALC)/ACC	CALCULATED	OBS	CALC	(OBS-CALC)/ACC	OBS	CALC	(OBS-CALC)/ACC
386	1	0	10.300			3.330	.009			..114		
387	2	468	10.700	10.141	2.23	3.247	.047	.074	-.39	.112	.115	-.07
388	3	1176	10.500	9.888	2.45	3.127	.111	.149	-.56	.153	.135	.41
389	4	2352	10.400	9.457	3.77	2.939	.200	.238	-.57	.201	.185	.36
390	5	11460	8.000	6.103	7.59	1.856	.562	.419	2.12	.575	.584	-.19

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APPENDIX E

ANALYTICAL METHODS

Formaldehyde and Formate Ion

The method used to determine formaldehyde was similar to the work of Dolzine, et al. [15]. According to this method, the unknown formaldehyde solution is added to an excess of bisulfite solution to form the anion formaldehyde-bisulfite, which can be measured by conductivity using IC (ion chromatography) and related back to the formaldehyde originally present in the sample. Technically, our previous work [1] revealed that the unreacted bisulfite ion is what is actually measured, not the formaldehyde-bisulfite ion; however, this had no effect on the accuracy of the data.

The advantage of this method for our application was that additional amounts of sodium bisulfite could be used to neutralize excess hydrogen peroxide from the reaction solution, thus stopping the reaction in time, since the neutralization of peroxide is very fast with bisulfite. Next, following the method of Dolzine, excess bisulfite (not the formaldehyde-bisulfite ion) is destroyed by the careful addition of peroxide just before IC analysis.

The IC instrument used for our analyses was the Dionex model 2120i. The procedures used and the accuracies achieved are described in [1].

Stock formaldehyde solutions were assayed according to the titrametric sodium sulfite method. The method is based on the quantitative liberation of sodium hydroxide when formaldehyde reacts with sodium sulfite.

The IC method was also used to determine formate ion concentration. The same injection for formaldehyde gave the characteristic retention time for the formate ion. Using internal and external standards, formate ion was quantitated for the reactor samples. Stock formate solution concentrations were based on the assay given for the ACS (American Chemical Society) grade formic acid.

Carbon-14 Studies

The carbon atom of the formaldehyde molecule can be followed in the reaction by the addition of a small amount of radioactive formaldehyde. This ^{14}C atom emits a charcteristic beta particle that reacts with the scintillation solution to cause light that is recorded
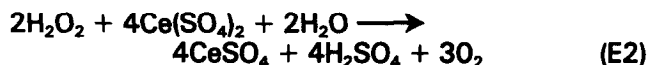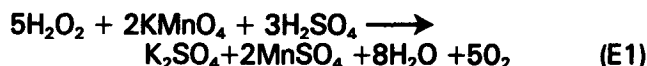
by a liquid scintillation counter. A reaction solution of 0.5 mL was introduced into 10 mL of a liquid cocktail for scintillation counting. The ^{14}C counts measured the number of soluble ^{14}C compounds that had radioactive formaldehyde as starting material.

Total Iron

Iron in the test solutions was determined by atomic absorption spectroscopy. Samples were acidified (0.1 percent HCl) and determined with background correction. Standards and blanks were used throughout the test and recoveries were performed. Accuracy was estimated to be 0.002 mmol/L.

Hydrogen Peroxide

Of the various methods in the literature for hydrogen peroxide determination only permanganate and ceric sulfate titrations were considered appropriate for the reaction under study. Almost all colorimetric methods were ruled out based on the interference from iron. The following reactions were considered:

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \longrightarrow$$
$$K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2 \qquad (E1)$$

$$2H_2O_2 + 4Ce(SO_4)_2 + 2H_2O \longrightarrow$$
$$4CeSO_4 + 4H_2SO_4 + 3O_2 \qquad (E2)$$

Reaction (E1) represents the permanganate method [12], in which the purple permanganate ion, MnO_4^{-2}, is reduced to the almost clear manganese ion, Mn^{+2}. Reaction (E2) represents the ceric method [16], in which the yellow ceric ion, Ce^{+4}, is reduced to the clear cerous ion, Ce^{+2}.

Based on the following series of tests it appears that, for our test conditions, ceric sulfate is the better of the two methods for hydrogen peroxide determination. It was found that the permanganate titrations were interfered with by other organics in the test solutions; whereas, the ceric sulfate titrations were unaffected. Accuracy for the ceric sulfate method was estimated to be 0.250 mmol/L.

Tests to Determine Adequacy of Titrametric Methods

Test 1. – The following test shows the failure of permanganate as a selective oxidant for hydrogen

peroxide because organics known to be present in the reaction solution interfere. The test shows that ceric ion is selective towards the oxidation of hydrogen peroxide in the presence of methyl alcohol, formaldehyde, and formate ion.

Test Procedure:

1) Add 25 mL of 1.0 N H_2SO_4 to eight 125-mL Erlenmeyer flasks.

2) Label four of the Erlenmeyer flasks "permanganate study" and the other four "ceric study."

3) Using the four "permanganate study" flasks:
   Label and add 25 mL of deionized water to the first flask
   Label and add 25 mL of 1-percent methanol to the second flask
   Label and add 25 mL of 1-percent formaldehyde to the third flask
   Label and add 25 mL of 1-percent formic acid to the fourth flask

4) Repeat the above procedure for the "ceric study" flasks.

5) Add 0.05 mL of 0.5 N permanganate to produce the purple color for the four "permanganate study" flasks.

6) Add 0.05 mL of 0.25 N ceric sulfate to produce the yellow color for the four "ceric study" flasks.

Table E-1 shows that, for the permanganate flasks, the color development varies depending on the organic added; whereas, for the ceric flasks, color development is uniform, i.e. not affected by the organic additions.

Tests 2 through 5. – Additional tests were performed using the ceric sulfate method. The data shown in table E-2 provide information on the precision of the titration and the effectiveness of acid as a means of "freezing" the reaction.

Each test represents formaldehyde oxidation using the conditions set forth in test 10 (phase I testing), referred to as "midpoint conditions." After waiting the designated time, the reaction was "frozen" by adding sufficient sulfuric acid to make the solution

Table E-1. – Comparative effects of organics on the permanganate and ceric sulfate titration methods for hydrogen peroxide analysis.

Test solution	Titration color development	
	Permanganate method	Ceric sulfate method
Blank	purple	yellow
Methanol	pink (<60 min)	yellow
Formaldehyde	clear (<1 min)	yellow
Formic acid	clear (<30 min)	yellow

Note: Duration of the test was 5 hours.

1.0 N. This was the amount of acid recommended for the ceric titration. After acid was added to the reactor, sampling continued for approximately 17 hours (1,020 minutes). This was to verify the effectiveness of the acid as a means of freezing the reaction in time. Each additional test allowed the reaction to proceed as defined in test 10, before acid addition.

Conclusions drawn based on the results of tests 2 through 5 are that the endpoint is sharp and good precision should be realized, no additional peroxide is used by organics after fixing the reaction with sulfuric acid, and the acid causes the reaction to slow to such a rate that analysis could be performed the next day (not recommended however).

Test 6. – After the addition of sulfuric acid, the 120-minute sample from the reactor produced more gas than the other samples. Test 6 was designed to determine whether a rapid loss of peroxide occurred because of decomposition or whether the gas observed was simply carbon dioxide (reaction was not stirred).

The results of test 6, shown in table E-3, indicate no peroxide loss as a result of decomposition when the pH is adjusted with sulfuric acid to 1.0 N.

Note that 0.01-percent hydrogen peroxide was left in the reaction after 120 minutes for test 5, whereas 0.33-percent hydrogen peroxide was left after 120 minutes for test 6. Since the only significant difference between the two tests was that different beakers were used, scratches inside the beakers probably account for peroxide loss.

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Table E-2. – Results of tests to determine the precision of the ceric sulfate titration method.

Test No.	Reaction time, minutes	Sample time, minutes	Sample size, mL	Ceric Sulfate, mL	Percent H_2O_2
2	0.5	1	10	7.9	0.336
		1	10	8.0	.340
		1	10	8.0	.340
		15	10	7.9	.336
		15	10	8.05	.342
		15	10	8.0	.340
		30	10	7.9	.336
		30	10	8.0	.340
		30	10	8.0	.340
		60	10	7.95	.338
		60	10	7.95	.338
		60	10	8.0	.340
		120	10	7.9	.336
		120	10	7.9	.336
		120	10	7.9	.336
		1020	10	7.85	.334
		1020	10	7.85	.334
		1020	10	7.83	.333
3	10	5	20	15.55	.330
		5	20	15.60	.332
		5	20	15.45	.328
		210	20	15.0	.319
		210	20	14.95	.318
		210	20	15.05	.328
		1160	20	14.9	.317
		1160	20	15.0	.319
		1160	20	15.0	.319
4	40	5	20	12.5	.266
		5	20	12.5	.266
		5	20	12.6	.268
		170	20	12.5	.266
		170	20	12.55	.267
		170	20	12.6	.268
		1130	20	12.5	.266
		1130	20	12.55	.267
		1130	20	12.5	.266
5	120	5	20	2.5	.053
		5	20	2.4	.051
		5	20	2.45	.052
		90	20	2.3	.049
		90	20	2.4	.051
		90	20	2.4	.051
		1050	20	–	–
		1050	20	2.3	.049
		1050	20	2.3	.049

Table E-3. – Recovery of peroxide before/after acidification.

Test condition	Ceric sulfate (mL)	Percent H_2O_2
Combine 1.0 L of H_2O with 5.0 mL of 30-percent H_2O_2	8.15 8.20 8.20	0.173 .174 .174
Combine 1.0 L of 120-minute reaction solution with 5.0 mL of 30-percent H_2O_2 (peroxide added just before acidification)	16.2 16.35 16.45	.344 .347 .350
1.0 L of 120-minute reaction solution	8.2 8.3 8.3	.174 .176 .176
Combine 1.0 L of 120-minute reaction solution with 5.0 mL of 30-percent H_2O_2 (peroxide added after acidification)	16.35 16.4 16.45	.347 .349 .350

Mission of the Bureau of Reclamation

The Bureau of Reclamation of the U.S. Department of the Interior is responsible for the development and conservation of the Nation's water resources in the Western United States.

The Bureau's original purpose "to provide for the reclamation of arid and semiarid lands in the West" today covers a wide range of interrelated functions. These include providing municipal and industrial water supplies; hydroelectric power generation; irrigation water for agriculture; water quality improvement; flood control; river navigation; river regulation and control; fish and wildlife enhancement; outdoor recreation; and research on water-related design, construction, materials, atmospheric management, and wind and solar power.

Bureau programs most frequently are the result of close cooperation with the U.S. Congress, other Federal agencies, States, local governments, academic institutions, water-user organizations, and other concerned groups.